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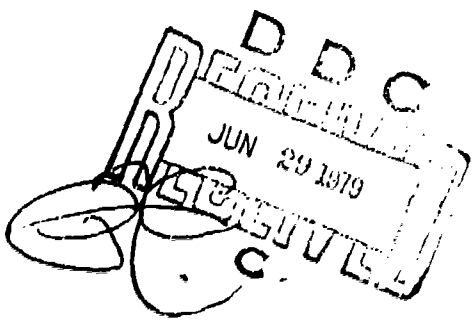
ANALYSIS OF AIRCRAFT FUELS AND RELATED MATERIALS

F. Neil Hodgson and John D. Tobias

MONSANTO RESEARCH CORPORATION
DAYTON LABORATORY
DAYTON, OHIO 45407



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R. D. BUTLER
Project Scientist

A. V. CHURCHILL
Chief, Fuels Branch

FOR THE COMMANDER

B. C. DUNNAM
Chief, Fuels and Lubrication Division

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The physical properties of a series of JP-9 fuels, whose compositions covered the entire range allowed by the fuel specification, were determined. Included in the study are density, viscosity, surface tension, vapor pressure, specific heat, thermal conductivity, dielectric constant, air/nitrogen/water solubility, heat of combustion and freeze point. A proposed gas chromatographic method for the analysis of JP-9 fuel has been validated and results are reported.

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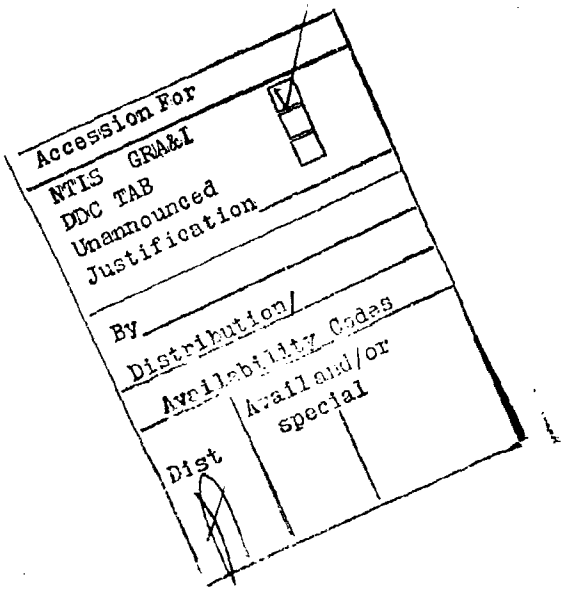
A survey of methods for hydrocarbon type analysis in fuels was conducted. Specific NMR approaches to this kind of analysis were applied to jet fuels and are presented. Analytical data are reported to determine the effect on combustion of modifying various fuels. A number of special studies which were conducted to aid in the solution of Air Force operational problems were conducted and are reported.



FOREWORD

This final report was submitted by Monsanto Research Corporation, under Contract F33615-76-C-2014. The effort was sponsored by the Air Force Aero Propulsion Laboratory, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio under Project Number 3048, Task number 304805 and Work Unit 30480574 with Dr. Ronald D. Butler/SFF as Project Monitor. Mr. F. Neil Hodgson of Monsanto Research Corporation was technically responsible for the work which was performed during the period 1 February 1976 - 31 August 1978 and submitted by the authors in January 1979.

Much of the work performed during the course of this program was planned in coordination with a number of other, related fuel technology studies being conducted at, or under the sponsorship of, the Air Force Aero Propulsion Laboratory. Such efforts include research on turbine engine combustor design, fuel combustion behavior, improved fuel characterization methodology, high density missile fuel development, and alternate fossil fuel source development. The experimental results presented in this report are intended to be used in the context of those research programs, and it is expected that the significance of the data will become apparent as the technical aspects of the related programs are published. In particular, many of the fuel specimens examined during this program were experimental in nature, and the various chemical and physical properties tabulated herein should not necessarily be regarded as characteristic of particular fuel types.

The authors wish to gratefully acknowledge the excellent guidance and counsel provided by Dr. Butler during the course of this work. Special gratitude is also expressed to members of the Monsanto Research Corporation staff: J. V. Pustinger for his technical consultation and advice and J. E. Strobel, C. D. Fritsch, R. C. Gable and A. M. Kemmer (formerly of MRC) for their technical assistance. H. Luebke and O. P. Tanner, Monsanto Company, St. Louis, are also recognized for the special data they have provided for this program.

In addition to the effort described in this report, work on the construction and feasibility testing of a prototype U.V. photometric detector for gas chromatography was conducted under the program. This work is described in a separate technical report entitled "An Ultraviolet Photometric Detector for Use in Gas Chromatography" (November 1977), AFAPL-TR-77-60.

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SECTION I

INTRODUCTION AND SUMMARY

The research and development work described in this technical report was conducted to aid in the solution of Air Force fuels related operational problems, to furnish information for use in Air Force in-house and contractual research programs, to provide data for development of advanced fuels and fuel specifications, and to investigate new approaches for the characterization of conventional and experimental fuels.

A number of investigations were conducted on high density fuels and fuel blends. These included a program in which detailed measurements were conducted for a number of chemical and physical properties on a series of fuels covering the entire JP-9 composition range.

Proposed methodology for the analysis of the high density fuel, JP-9, was validated in a cooperative study with Air Force scientists. Isomers of the major JP-9 constituent, hydrogenated norbornadiene (RJ-5), were separated by preparative gas chromatography and enthalpies of fusion for each were measured. Numerous other measurements of a support nature were conducted on high density fuels during the course of this program.

A number of special investigations were conducted. Included in these was a study of hydrocarbon emissions from vapor-containing 50,000 gallon fuel storage tanks as they were filled with JP-4. A potential non-flammable replacement for test fluid Mil-F-7024B was evaluated by examining such properties as engine seal compatibility, evaporation loss, viscosity and lubricity.

In support of Air Force fuel combustion programs, a large number of fuel specimens were physically and chemically characterized. This analytical effort involved both conventional and modified fuels with both chemical and physical characterization being performed.

A critical survey of methods for hydrocarbon type analysis of aircraft fuels was conducted. The purpose of the survey was to determine how the various methods of hydrocarbon type analysis differ and to identify those methods which give results that best correlated with fuel combustion properties. Several methods were tested for their applicability to jet fuels.

These and other studies required for research support or problem solving are described in the following sections.

SECTION II

HIGH DENSITY FUELS CHARACTERIZATION

The special high-density propellant, JP-9, has been the subject of intense developmental effort within the Air Force Aero Propulsion Laboratory during the period covered by this program. The fuel, because of its unusually high density compared to conventional jet fuels, has a high volumetric heat of combustion. This characteristic allows the fuel to provide a greater flight range than can be obtained with conventional fuels, without increasing the fuel volume. The advantage is of critical importance in volume-limited missile systems such as the air-launched cruise missile (ALCM) and the advanced strategic air-launched missile (ASALM).

A large number of the investigations and studies conducted under this program were related to Air Force Aero Propulsion Laboratory experimental work on JP-9 and its components. This work involved the development of fuel specifications, verification of analytical protocol, development of fuel data for the engineering of the individual missile systems and a variety of related projects.

Tasks relating largely to the physical properties of JP-9 and its constituents are presented in this section.

1. ENGINEERING DATA ON JP-9 FUELS AND FUEL COMPONENTS

In support of the Air Force high density fuel development program, engineering data essential for the development of specific USAF missile systems were generated on JP-9 fuel. Blends of the fuel components were prepared which covered but did not exceed the specified composition range for JP-9 fuel. The current specification for this fuel establishes its composition as:

	wt. %
methylcyclohexane (MCH)	10-12
exo-tetrahydrodi(cyclopentadiene), exo-THD	65-70
RJ-5	20-25

In cases where useful calculations or predictions of fuel properties were possible from data on individual components, properties were measured on each pure component as well as on blended fuels.

Three fuel blends were prepared from each of four different batches of RJ-5. The composition of these fuels are given in Table 1.

TABLE 1. COMPOSITION OF PREPARED TEST FUELS

	Weight Percent			
Fuel No.	MCH	exo-THD	RJ-5	RJ-5 Lot or Batch
JP-9 #1	10.0	70.0	20.0	exo-endo
#2	10.0	70.0	20.0	Batch 3
#3	10.0	70.0	20.0	Lot 10704-67A
#4	10.0	70.0	20.0	11410-104
#5	10.0	65.0	25.0	exo-endo
#6	10.0	65.0	25.0	Batch 3
#7	10.0	65.0	25.0	Lot 10704-67A
#8	10.0	65.0	25.0	11410-104
#9	12.0	67.0	21.0	exo-endo
#10	12.0	67.0	21.0	Batch 3
#11	12.0	67.0	21.0	Lot 10704-67A
#12	12.0	67.0	21.0	11410-104

Kinematic Viscosity

Kinematic viscosity was determined as a function of temperature for all fuels and fuel components using the procedure described in ASTM D445. Viscosity data, presented in Table 2, are plotted on ASTM Standard viscosity-temperature charts and are shown in Appendix 1. These charts are useful for estimating kinematic viscosity at temperatures other than those for which measurements were conducted. It will be noted that none of the plots is linear over the entire temperature span. This is true for all fuels and pure exo-THD but not for the pure RJ-5 specimens which exhibit linear plots.

Fuels were observed to become cloudy, apparently due to the formation of a dispersed solid phase, at approximately -30°F and to a greater extent at -65°F. All fuels exhibited thixotropic behavior at -65°F resulting in viscosity changes produced solely by mechanical agitation. As a result, the efflux time varied for each replicate of the measurement. The measurement at -65°F was thus discontinued after being conducted on the first four fuels. For these fuels, the average of three consecutive measurements at -65°F are reported in each case.

Density as a Function of Temperature

The density of each fuel and fuel component was determined at four different temperatures using the dilatometer technique. Equations for temperature-density relationship were then computed by a least squares linear regression and are presented in Table 3. Correlation coefficients of 0.9999 were obtained in all cases. Measured and calculated density values over the -65°F to 160°F temperature range are presented in Table 4.

TABLE 2. KINEMATIC VISCOSITY

Fuel No.	-65°F	-30°F	0°F	32°F	77°F	155°F
			Centistokes			
JP-9 #1	41.06	16.42	9.092	5.350	3.076	1.534
#2	43.68	17.14	9.513	5.548	3.184	1.570
#3	43.00	17.06	9.341	5.545	3.138	1.558
#4	42.30	16.93		5.477	3.148	1.556
#5		18.19		5.715	3.245	1.594
#6		19.56		6.053	3.411	1.648
#7		19.18		5.961	3.353	1.634
#8		19.03		5.934	3.346	1.630
#9		15.57		5.149	2.978	1.495
#10		16.52		5.397	3.099	1.537
#11		16.50		5.323	3.057	1.523
#12		16.34		5.325	3.066	1.526
RJ-5,Exo-Endo		743.8		51.36	17.19	5.112
RJ-5,10704-67a		1082		67.25	21.28	5.875
RJ-5, Batch 3		1432		78.79	24.01	6.423
RJ-5,11410-104		1008		65.78	21.13	5.919
Exo-THD		14.55		5.001	2.957	1.492
MCH	3.796	2.358		1.235	0.881	0.562

TABLE 3. EQUATIONS EXPRESSING TEMPERATURE/DENSITY RELATIONSHIP

Fuel or Component	Equation for Density at Temperature, $T_F°$	Correlation Coefficient
MCH	$D= -0.0004830T_F+0.80217$	0.9999
exo-THD	$D= -0.0004391T_F+0.96407$	0.9999
RJ-5 Exo-Endo	$D= -0.0004274T_F+1.10231$	0.9999
RJ-5, Batch 3	$D= -0.0004268T_F+1.10876$	0.9999
RJ-5, 10704-67a	$D= -0.0004378T_F+1.10203$	0.9998
RJ-5, 11410-104	$D= -0.0004278T_F+1.10595$	0.9999
JP-9 #1	$D= -0.0004290T_F+0.96925$	0.9999
#2	$D= -0.0004316T_F+0.97018$	0.9999
#3	$D= -0.0004365T_F+0.96915$	0.9999
#4	$D= -0.0004349T_F+0.96944$	0.9999
#5	$D= -0.0004320T_F+0.97092$	0.9999
#6	$D= -0.0004336T_F+0.97696$	0.9999
#7	$D= -0.0004447T_F+0.97644$	0.9999
#8	$D= -0.0004358T_F+0.97655$	1.000
#9	$D= -0.0004381T_F+0.96725$	0.9999
#10	$D= -0.0004431T_F+0.96870$	0.9999
#11	$D= -0.0004359T_F+0.96650$	0.9999
#12	$D= -0.0004403T_F+0.96788$	0.9999

TABLE 4. HIGH DENSITY FUEL DENSITIES AT VARIOUS TEMPERATURES

Fuel or Fuel Component	Density G/cc				
	-65°F*	-30°F	32°F	77°F	155°F
MCH	0.8335	0.8167	0.7867	0.7650	0.7273
Exo-THD	0.9926	0.9772	0.9500	0.9303	0.8960
RJ-5, Exo, Endo	1.1301	1.1151	1.0887	1.0693	1.0361
RJ-5, Batch 3	1.1365	1.1216	1.0951	1.0759	1.0426
RJ-5, 10704-67a	1.1305	1.1152	1.0879	1.0685	1.0341
RJ-5, 11410-104	1.1338	1.1188	1.0922	1.0731	1.0396
JP-9 #1	0.9971	0.9821	0.9556	0.9361	0.9028
#2	0.9982	0.9831	0.9564	0.9369	0.9033
#3	0.9975	0.9822	0.9552	0.9355	0.9015
#4	0.9977	0.9825	0.9553	0.9363	0.9019
#5	1.0030	0.9879	0.9610	0.9418	0.9079
#6	1.0051	0.9900	0.9630	0.9437	0.9097
#7	1.0053	0.9898	0.9622	0.9422	0.9075
#8	1.0049	0.9896	0.9626	0.9430	0.9090
#9	0.9957	0.9804	0.9535	0.9341	0.8995
#10	0.9975	0.9820	0.9545	0.9340	0.9000
#11	0.9948	0.9796	0.9525	0.9330	0.8989
#12	0.9965	0.9811	0.9539	0.9338	0.8997

* Calculated from equations, Table 3.

Heat of Combustion

Heat of combustion values for the JP-9 fuels and their components were determined according to ASTM D240, employing the oxygen bomb calorimeter. Net values were calculated from the gross heat of combustion using the equation

$$H_n = H_g - 91.23H \quad (1)$$

where H_n = net heat of combustion
H_g = gross heat of combustion
H = percent of hydrogen in sample

The percent hydrogen was calculated from the known compositions. Duplicate determinations were conducted for all samples. Values are presented in Table 5.

Dielectric Constant

Dielectric constants were measured for all fuels and fuel components as a function of temperature at 400 Hz. Measurements were made in a three terminal guarded cell relative to air at the same temperature. A General Radio 1615A capacitance bridge and guard circuit were used for the work. Raw data are presented in Table 6. Linear equations generated by linear regression treatment of the data are presented in Table 7.

Surface Tension

Surface tension was measured as a function of temperature using the capillary-rise method described in Appendix B.

The contact angle was found to be zero, thus cos θ is equal to one for all samples excepting the RJ-5 fuels. For those materials contact angle corrections were made. Data could not be obtained for RJ-5 at the lower temperatures of -32°F due to its

TABLE 5. HEAT OF COMBUSTION OF HIGH DENSITY FUELS

Fuel or Fuel Component	Gross BTU/lb.	Net BTU/lb.	Net Cal/G
RJ-5, 10704-67a	18,802 18,812 Av. 18,807	17,836	9,909
RJ-5, Batch 3	18,731 18,754 Av. 18,733	17,772	9,873
RJ-5, Exo-Endo	18,722 18,759 Av. 18,741	17,858	9,921
RJ-5, 11410-104	18,804 18,760 Av. 18,782	17,811	9,895
Exo-THD	19,166 19,146 Av. 19,156	18,083	10,046
MCH*	19,968 20,008 Av. 19,989	18,700	10,389
JP-9, #1	19,026 19,043 Av. 19,035	17,976	9,987
JP-9, #2	18,942 18,943 Av. 18,943	17,867	9,926
JP-9, #3	19,014 19,069 Av. 19,042	17,966	9,981
JP-9, #4	19,009 18,986 Av. 18,998	17,922	9,956
JP-9, #5	19,010 19,070 Av. 19,040	17,992	9,995
JP-9, #6	18,993 18,955 Av. 18,974	17,904	9,946
JP-9, #7	18,768 19,003 Av. 18,786	17,815	9,897
JP-9, #8	18,979 19,005 Av. 18,992	17,922	9,959
JP-9, #9	19,077 19,054 Av. 19,066	18,005	10,003
JP-9, #10	18,957 18,976 Av. 18,967	17,888	9,937
JP-9, #11	19,056 19,112 Av. 19,084	18,006	10,003
JP-9, #12	19,041 19,017 Av. 19,029	17,951	9,972

*Reported previously, Report 74-41, 14 October 1974, Contract F33615-74-C-2002.

TABLE 6. DIELECTRIC CONSTANTS OF HIGH DENSITY FUELS

Sample	-65°F	32°F	72.5°F	156°F
JP-9 #1	2.622	2.535	2.501	2.425
#2	2.624	2.534	2.502	2.422
#3	2.643	2.545	2.495	2.413
#4	2.640	2.547	2.505	2.425
#5	2.639	2.547	2.512	2.432
#6	2.628	2.547	2.515	2.444
#7	2.640	2.547	2.511	2.428
#8	2.637	2.544	2.507	2.426
#9	2.579	2.506	2.461	2.404
#10	2.560	2.496	2.465	2.412
#11	2.552	2.495	2.459	2.415
#12	2.563	2.490	2.455	2.394
RJ-5, Batch 3	2.782	2.728	2.698	2.654
RJ-5, 10704-67a	2.773	2.703	2.670	2.611
RJ-5, Exo-Endo	2.824	2.730	2.691	2.610
RJ-5, 11410-104	2.822	2.730	2.691	2.612
exo-THD	2.554	2.489	2.463	2.407
MCH	2.129	2.055	2.024	1.960

TABLE 7. EQUATIONS FOR CALCULATION OF DIELECTRIC CONSTANT AT TEMPERATURE, $T_F°$

Sample	Equation*
JP-9 #1	$\epsilon = -0.0008905\ T_F° + 2.564$
#2	$\epsilon = -0.0009114\ T_F° + 2.565$
#3	$\epsilon = -0.00105\ T_F° + 2.575$
#4	$\epsilon = -0.00098\ T_F° + 2.577$
#5	$\epsilon = -0.00093\ T_F° + 2.578$
#6	$\epsilon = -0.0008336\ T_F° + 2.574$
#7	$\epsilon = -0.0009561\ T_F° + 2.578$
#8	$\epsilon = -0.0009544\ T_F° + 2.575$
#9	$\epsilon = -0.0008016\ T_F° + 2.527$
#10	$\epsilon = -0.0006710\ T_F° + 2.516$
#11	$\epsilon = -0.0006274\ T_F° + 2.511$
#12	$\epsilon = -0.0007676\ T_F° + 2.513$
RJ-5, 10704-67a	$\epsilon = -0.0007366\ T_F° + 2.725$
RJ-5, Batch 3	$\epsilon = -0.0005863\ T_F° + 2.744$
RJ-5, Exo-Endo	$\epsilon = -0.0009681\ T_F° + 2.761$
RJ-5, 11410-104	$\epsilon = -0.0009507\ T_F° + 2.760$
exo-THD	$\epsilon = -0.0006706\ T_F° + 2.511$

* $T_F°$ = Temperature in °F
  ϵ = Dielectric Constant

high viscosity and poor wetting of the glass. The linear temperatures/surface tension relationship, however, was established using measurements at higher temperatures. Surface tension values are presented in Table 8, and surface equations are shown in Table 9.

Freeze Point

Freeze point measurements were conducted using the apparatus and procedure described in ASTM D2386. None of the fuels showed a freeze point upon being cooled to -70°F. However, the turbidity or dispersed solid phase, as discussed under the section on viscosity, was once again observed.

Air Solubility

The amount of air which dissolves in JP-9 fuel at saturation was measured using the procedure described in Appendix B. Solubility is expressed by an Ostwald coefficient which is defined as the volume of air per unit volume of fuel, both measured at the temperature of saturation. Air solubility data are presented in Table 10.

Thermal Conductivity

Thermal conductivity by the transient hot wire method (1) was measured for the JP-9 fuels. In this procedure a constant heating current is applied abruptly to a resistance wire immersed in the fuel. The change in temperature of the wire following application of the current is obtained from the observed change of voltage across the wire and the known resistance-temperature characteristics. Data are presented in Table 11 and Figure 1.

TABLE 8. SURFACE TENSION AT VARIOUS TEMPERATURES

Fuel or Fuel Component	Surface Tension, dyne cm^{-1}					
	-65°F*	-30°F	32°F	72°F	158°F	190°F
MCH	32.843	30.806		24.465	19.519	
EXO-THD	37.850	35.928	32.926	30.534	26.097	
RJ-5, EXO-ENDO	33.710	33.365*		32.366	31.497	31.211
RJ-5, Batch 3	48.124	46.439*		41.537	37.347	35.872
RJ-5, 10704-67a	38.008	37.200*		34.872	32.762	32.193
RJ-5, 11410-104	41.068	39.838*		36.253	33.212	32.109
JP-9 #1	34.586	33.366*	31.230	29.776	26.826	
#2	39.989	38.212*	35.078	33.016	28.675	
#3	39.606	37.912		32.967	28.806	
#4	38.541	36.832	34.020	32.227	28.017	
#5	32.472	31.611*	30.103	29.076	26.994	
#6	40.444	38.541*	35.037	33.192	28.259	
#7	39.644	37.748	34.947	33.132	28.485	
#8	38.990	37.328		32.766	28.640	
#9	32.668	31.839		29.530	27.478	
#10	40.268	38.333*	34.951	32.628	27.961	
#11	39.222	37.432		31.928	27.573	
#12	38.646	37.226		31.199	27.995	

* Calculated from linear equations.

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#11	39.222	37.432		31.928	27.573	
#12	38.646	37.226		31.199	27.995	

* Calculated from linear equations.

TABLE 9. EQUATIONS FOR SURFACE TENSION OF JP-9 FUELS AT TEMPERATURE $T_F°$

Fuel or Fuel Component	Equation
MCH	$*\tau = -0.06010\ T_F° + 28.93684$
EXD-THD	$\tau = -0.05267\ T_F° + 34.42629$
JP-9 #1	$\tau = -0.03485\ T_F° + 32.32081$
#2	$\tau = -0.05076\ T_F° + 36.68966$
#3	$\tau = -0.04844\ T_F° + 36.45750$
#4	$\tau = -0.04689\ T_F° + 35.49348$
#5	$\tau = -0.02460\ T_F° + 30.87279$
#6	$\tau = -0.05436\ T_F° + 36.91019$
#7	$\tau = -0.05436\ T_F° + 36.43843$
#8	$\tau = -0.04617\ T_F° + 35.98914$
#9	$\tau = -0.02318\ T_F° + 31.16098$
#10	$\tau = -0.05528\ T_F° + 36.67480$
#11	$\tau = -0.05249\ T_F° + 35.81021$
#12	$\tau = -0.04941\ T_F° + 35.43385$

* Surface tension in dyne cm^{-1}.

TABLE 10. SOLUBILITY OF AIR IN JP-9 FUELS

Fuel	Ostwald Solubility Coefficients* -60°F	72°F	140°F
JP-9, #1	0.093	0.128	0.137
JP-9, #2	0.095	0.126	0.141
JP-9, #3	0.096	0.126	0.138
JP-9, #4	0.086	0.122	0.148
JP-9, #5	0.090	0.126	0.149
JP-9, #6	0.091	0.125	0.146
JP-9, #7	0.094	0.117	0.145
JP-9, #8	0.092	0.121	0.148
JP-9, #9	0.089	0.110	0.133
JP-9, #10	0.091	0.114	0.144
JP-9, #11	0.092	0.125	0.146
JP-9, #12	0.094	0.133	0.149

* ml of air/ml of fuel both measured at the temperature of saturation

TABLE 11. THERMAL CONDUCTIVITY OF JP-9 FUEL BLENDS

Sample No.	Thermal Conductivity, BTU/ft/hr°F -40°F	68°F	150°F
JP-9 #1	0.07068	0.06543	0.06216
JP-9 #2			0.06143
JP-9 #3	0.06975	0.06495	0.06147
JP-9 #7	0.06825	0.06486	0.06093
Toluene Std.	0.08649	0.07624	
Toluene, (literature)	0.08684	0.07745	

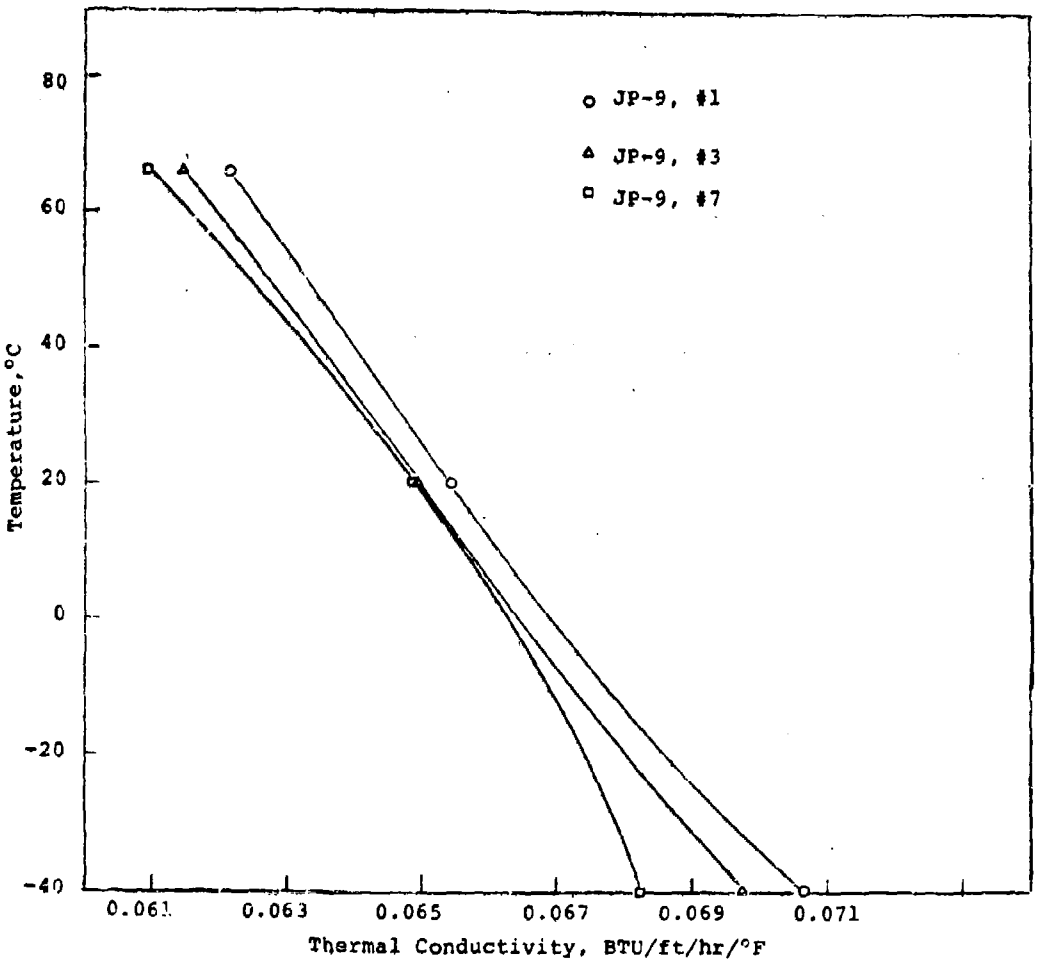

Figure 1. Thermal conductivity as a function of temperature for JP-9 fuels.

Specific Heat

Specific heats of the fuels and their components were determined by means of a Perkin Elmer DSC-2 differential scanning calorimeter using the Intracooler II, Scanning AutoZero and Programmable Calculator accessories. Samples were hermetically sealed in aluminum volatile-sample pans, inside a controlled atmosphere box purged with dry nitrogen. Continuous scans, at 5°C/min were made from -60° to 70°C and data [illegible] off at -40°, 20° and 66°C to generate the data shown in Table 12. Repeat measurements and the sapphire* reference data indicate accuracy and average precision figures of about ±2% or better. The results for the n-octane reference fluid indicate good accuracy through averaging. The twenty-nine scans were made over a five-day period. Since samples could not all be run in a continuous unit of time, measurement errors were randomized by non-sequential ordering and repeating some sample scans. The overall result should be improved absolute accuracy, since we also standardized with the sapphire reference material on a daily basis. The n-octane reference sample was run to reference the data to published values. Excellent agreement with two sources (2, 3), as listed in Table 12, was found.

Nitrogen Solubility

The amount of nitrogen which dissolves in JP-9 fuels at saturation was determined using the apparatus described in Appendix B for air solubility measurements. The basic measuring device was a CEC-21-103 mass spectrometer. Ostwald nitrogen solubility coefficients were calculated and are presented in Table 13.

*Sapphire is commonly used as a reference material for thermal measurement.

TABLE 12. SPECIFIC HEAT VALUES FOR JP-9 FUELS AND COMPONENTS

Fuel No.	Specific Heat in Cal/g°c or BTU/lb°F -40°F (-40°C)	68°F (20°C)	150°F (66°F)
JP-9 #1	0.305	0.364	0.414
	0.312	0.369	0.421
	0.315	0.371	0.421
	0.322	0.380	0.431
	Average 0.314	Average 0.371	Average 0.422
#2	0.300	0.364	0.411
	0.310	0.364	0.422
#3	0.305	0.359	0.408
#4	0.311	0.372	0.422
#5	0.316	0.367	0.420
#6	0.312	0.361	0.413
#7	0.313	0.371	0.423
#8	0.298	0.363	0.404
	0.309	0.367	0.415
	0.316	0.384	0.427
	Average 0.308	Average 0.371	Average 0.415
MCH	0.387	0.440	0.488
	0.370	0.417	0.473
	0.415	0.492	0.562
	0.411	0.497	0.558
	0.394	0.460	0.515
	Average 0.395	Average 0.461	Average 0.519
exo-THD	0.318	0.376	0.425
	0.320	0.377	0.431
RJ-5 (Exo-Endo)	0.281	0.341	0.384
RJ-5 Batch 3	0.278	0.339	0.384
RJ-5 10704-67A	0.270	0.328	0.372
	0.275	0.346	0.390
RJ-5 11410-104	0.267	0.332	0.376
n-Octane Reference	0.457	0.504	0.550
	0.494	0.528	0.568
	0.488	0.532	0.576
	Average 0.480	Average 0.521	Average 0.565
Literature (Ref. 2)	0.482	0.523	0.561
Literature (Ref. 3)	0.4892	-	-

TABLE 13. SOLUBILITY OF NITROGEN IN JP-9 FUELS

Fuel	Ostwald Solubility Coefficients* -60°F	72°F	140°F
JP-9, #1	0.083	0.112	0.122
JP-9, #2	0.085	0.110	0.125
JP-9, #3	0.086	0.110	0.123
JP-9, #4	0.076	0.107	0.132
JP-9, #5	0.080	0.110	0.133
JP-9, #6	0.081	0.109	0.130
JP-9, #7	0.084	0.102	0.129
JP-9, #8	0.082	0.106	0.132
JP-9, #9	0.080	0.096	0.118
JP-9, #10	0.081	0.099	0.128
JP-9, #11	0.082	0.109	0.130
JP-9, #12	0.084	0.116	0.132

* ml of air/ml of fuel, both volumes measured at the temperature of saturation

Water Solubility

The amount of water which will dissolve in the test fuels was determined at various temperatures by ASTM D 1744-64 using a fully automatic Karl Fischer apparatus consisting of a Luft Model 77 solid state controller and a Luft Model A-KF Karl Fischer titrimeter. A 50-ml portion of each water-saturated fuel was taken for analysis. The fuels have densities close to that of water, making separation of phases by gravity difficult. Droplets of water were separated from the fuels by centrifugation prior to analysis. Data are presented in Table 14.

Vapor Pressure

Vapor pressures as a function of temperature were determined for the test fuels using the micromethod as described by Mottlau (4) and as presented in ASTM D 2551-71. A special vapor pressure apparatus was constructed (Lab Glass, Inc., Vineland, N.J.) which incorporates a mercury-sealed orifice sample introduction system. The results varied from those obtained by adhering strictly to ASTM Method D 2551 in that the final vapor pressure values do not include the partial pressure of dissolved air. Vapor pressures were measured as a function of temperature by circulating fluid from a constant temperature bath through the outer jacket of the apparatus. Data are presented in Table 15.

The vapor pressure of a sample may be expressed as a function of temperature by an equation of the form:

$$\log P = -A \left(\frac{1}{T}\right) + B \qquad (2)$$

where P = vapor pressure
T = temperature in degrees Kelvin
A and B are constants

TABLE 14. SOLUBILITY OF WATER IN JP-9 FUELS

Fuel	Water Content (parts per million, vol.) 32°F	72°F	150°F
JP-9 #1	37	49	62
#2	42	58	75
#3	25	46	71
#4	28	50	67
#5	35	55	81
#6	32	61	75
#7	29	42	68
#8	27	44	71
#9	31	49	79
#10	39	53	75
#11	30	43	80
#12	35	53	78

TABLE 15. VAPOR PRESSURE OF JP-9 TEST FUELS

Fuel No.	Pressure, torr			
	36°F	77°F	104°F	136°F
JP-9 #1	5.2	13	21	39
#2	4.5	11.5	19.5	37
#3	5.2	13	22	41.5
#4	4.5	11.5	19.5	37
#5	4.5	11	20	38.5
#6	4.9	11.5	18.5	38
#7	5.4	13	23	41
#8	4.6	11	19.5	38
#9	5.2	14	25	45.5
#10	5.5	14	24	43.5
#11	5.6	14.5	25	46.5
#12	5.2	14	26	45

Plots of log vapor pressure versus 1/T for the data in Table 15 show excellent linearity. Equations for calculating vapor pressure at intermediate temperatures have been computed using the least-square treatment of data. Equations are presented in Table 16.

2. AIR SOLUBILITY AND SURFACE TENSION OF JP-9 FUELS

Surface tension and air solubility are particularly important in establishing engine design criteria. These properties were measured as a function of temperature for JP-9 fuels which were formulated by weight to give component concentrations falling within specification ranges. RJ-5 samples from different sources were used for each fuel. Compositions are presented in Table 17.

Air Solubility

The amount of air which dissolves in JP-9 fuel at saturation was measured using the same procedure employed for previous similar measurements and described in Appendix B.

Air saturation values are presented in Table 18 in terms of gas volume (ml) dissolved in one gram of fuel. Ostwald coefficient, commonly used to express gas solubility, were calculated by multiplying each value by the fuel density at that temperature.

Surface Tension and Density

Surface tension was measured for each JP-9 specimen at three temperatures using the capillary rise method described in Appendix B. Density measurements as a function of temperature were made by the dilatometer technique. These values were used to calculate surface tension. Data are presented in Table 19.

TABLE 16. EQUATIONS FOR VAPOR PRESSURE AS A FUNCTION OF TEMPERATURE FOR JP-9 TEST FUELS

	Equation
JP-9 #1	$\log P = -1.4007 \left(\frac{1000}{T}\right) + 5.8140$
#2	$\log P = -1.4627 \left(\frac{1000}{T}\right) + 5.9737$
#3	$\log P = -1.4423 \left(\frac{1000}{T}\right) + 5.9606$
#4	$\log P = -1.4627 \left(\frac{1000}{T}\right) + 5.9737$
#5	$\log P = -1.4972 \left(\frac{1000}{T}\right) + 6.0899$
#6	$\log P = -1.4066 \left(\frac{1000}{T}\right) + 5.7946$
#7	$\log P = -1.4192 \left(\frac{1000}{T}\right) + 5.8921$
#8	$\log P = -1.4682 \left(\frac{1000}{T}\right) + 5.9922$
#9	$\log P = -1.5171 \left(\frac{1000}{T}\right) + 6.2397$
#10	$\log P = -1.4421 \left(\frac{1000}{T}\right) + 5.9887$
#11	$\log P = -1.4749 \left(\frac{1000}{T}\right) + 6.1163$
#12	$\log P = -1.5198 \left(\frac{1000}{T}\right) + 6.2517$

TABLE 17. JP-9 BLENDED COMPOSITIONS

Fuel	RJ-5 Source	Weight Percent		
		RJ-5	exo-THD*	MCH+
Blend 1	Ashdyne Drum 22	20.07	67.91	12.02
Blend 2	Ashland 10 May 1974	20.59	68.74	10.66
Blend 3	Sun Oil 743011	20.15	67.89	11.95

* exo-tetrahydrodi(cyclopentadiene)
\+ methyl cyclohexane

TABLE 18. SOLUBILITY OF AIR IN JP-9 FUELS

Fuel	Temperature T (°F)	ml of Air at T per gram of Fuel	Ostwald Solubility Coefficient*
Blend 1	-60°F	.091	.091
	76°F	.132	.123
	144°F	.165	.149
Blend 2	-60°F	.093	.093
	76°F	.134	.125
	144°F	.157	.142
Blend 3	-60°F	.094	.093
	76°F	.126	.118
	144°F	.145	.131

* ml of air/ml of fuel, both at temperature, T

TABLE 19. SURFACE TENSION AND DENSITY OF JP-9 FUELS

Fuel	Temperature (°F)	Surface Tension (Dynes cm^{-1})	Density (g/cc)
Blend 1	-30	35.41	0.9851
	72	30.77	0.9388
	143	27.53	0.9082
Blend 2	-30	35.63	0.9812
	72	30.83	0.9354
	143	27.47	0.9045
Blend 3	-30	35.49	0.9828
	72	30.48	0.9373
	143	26.98	0.9058

3. SURFACE TENSION AND HEAT OF COMBUSTION OF SPECIFIC RJ-5 ISOMERS AND ISOMER BLENDS

Surface tension as a function of temperature and heat of combustion were determined for three specially modified RJ-5 fuels consisting of the endo-endo isomer, the exo-exo isomer and a blend of each.

Surface tension was measured using the capillary-rise method described in Appendix B. Values are presented in Table 20 for each fuel. Densities are presented in Table 21. Heat of combustion values were measured by ASTM D-240 and are presented in Table 22.

4. FILTRATION, COMPOSITION, AND PROPERTIES MEASUREMENTS OF FOURTEEN HIGH DENSITY FUELS

A total of fourteen RJ-5 fuel samples were analyzed to determine purity, composition, freezing point and viscosity as a function of temperature. Nine of the samples (TMC-1 to -9) were fuels which had been returned to AFAPL/SFF by a contractor and were suspected of being contaminated with water and/or particulate matter.

Clay Filtration of Contaminated Fuels

The nine fuels suspected of contamination were examined by emptying the entire contents of each amber glass bottle into a large beaker. Six of the fuels were obviously contaminated as indicated by the following descriptions:

TABLE 20. SURFACE TENSION OF MODIFIED RJ-5 FUELS AS A FUNCTION OF TEMPERATURE

	Contact Angle (degrees)	Temp. (°F)	Surface Tension (Dynes cm^{-1})
Endo-Endo Isomer	35°	75°	46.89
		140°	43.82
		158°	43.03
		176°	42.39
Exo-Exo Isomer	32°	75°	44.68
		140°	41.49
		158°	40.72
		176°	39.86
Blend	34°	75°	45.96
		140°	42.58
		158°	41.75
		176°	40.85

TABLE 21. DENSITIES OF MODIFIED RJ-5 FUELS

	gms/cc			
	-30°F	+32°F	+72°F	+143°F
Exo-Exo Isomer	1.0890*	1.0770	1.0603	1.0297
Endo-Endo Isomer	1.1211	-	1.0772	1.0471
Blend	1.1148†	-	1.0704	1.0397

* sam ie solidified
† sample cloudy

TABLE 22. HEAT OF COMBUSTION OF MODIFIED RJ-5 FUELS

Sample		Gross		Net	
		BTU/lb	Cal/g	BTU/lb	Cal/g
Endo-Endo Isomer		18,707	10,393	17,824	9902
		18,678	10,377	17,795	9886
	Avg.	18,693	10,385	17,810	9894
Exo-Exo		18,773	10,429	17,890	9939
		18,782	10,434	17,899	9944
	Avg.	18,778	10,432	17,895	9941
Blend		18,749	10,416	17,866	9925
		18,767	10,426	17,884	9935
	Avg.	18,758	10,421	17,875	9931

Sample No.	Appearance of Fuel
TMC-2	Slightly turbid
TMC-3	Yellow and turbid
TMC-4	Brown scum with water droplets
TMC-7	Layer of water on top
TMC-8	Dark yellow and slightly turbid
TMC-9	Dark yellow

The remaining fuels in this lot (TMC-1, TMC-5 and TMC-6) appeared to be uncontaminated. The other five of the fourteen fuels appeared clear and uncontaminated.

The six contaminated fuels were treated by first removing as much water and scum as possible by decantation. Each fuel was then filtered through Attapulgus clay which had been preconditioned at 650°F for 45 minutes. All eluates were clear.

Chromatographic Analysis

The 14 samples were analyzed by gas chromatography using a Perkin-Elmer model 3920 gas chromatograph using instrument conditions A described in Appendix 2. Samples were diluted 50-fold with pentane and a 0.2 microliter aliquot was taken for analysis. Data were recorded using a Hewlett-Packard 3350 Lab Data System. Peak areas and area percents were recorded with the solvent peak being excluded. Due to the structural similarities of components, area percents can be assumed to be approximately equivalent to weight percents of the components in the original fuel. Chromatographic data for the fourteen fuels are presented in Table 23 where components having area percents of 0.5% or greater are tabulated along with their retention times. Typical chromatograms are shown in Figures 2-5. Two samples contain trace impurities which are not included in Table 23. These samples (7186-4 and 7186-5), shown in Figures 4 and 5, appear to have similar impurities.

TABLE 23. GAS CHROMATOGRAPHIC DATA FOR RJ-5 FUEL SAMPLES

Retention Time, Min.	Area Percent[a]													
	TMC-1	TMC-2	TMC-3	TMC-4	TMC-5	TMC-6	TMC-7	TMC-8	TMC-9	7186-1 TMC-10	7186-3 TMC-11	7186-2 TMC-12	7186-4[b] RJ-5F	7186-5[b] RJ-5G
6.02	-	-	-	-	4.80	-	-	0.56	0.64	-	-	-	-	-
6.29	-	-	-	-	-	-	0.59	-	-	-	-	-	-	-
9.70	-	-	-	1.25	-	-	-	-	-	-	-	-	-	-
10.52	-	-	-	2.88	-	-	-	-	-	-	-	-	-	-
13.90	0.84	0.90	1.06	1.05	0.95	0.98	0.59	0.82	.87	0.87	0.80	0.97	1.42	1.63
14.06	6.63	6.66	7.61	7.70	8.65	9.24	5.90	6.25	.29	7.08	6.66	6.93	1.38	2.13
14.33	15.73	16.04	16.64	17.65	16.34	19.44	14.04	14.97	..88	15.28	14.98	16.45	33.06	0.56
14.60	-	0.70	-	-	-	-	-	-	-	-	-	-	-	1.62
14.79	0.91	0.89	1.19	0.87	1.10	1.01	1.15	1.08	1.05	1.09	0.98	1.04	0.55	-
15.18	75.88	74.10	72.81	68.60	68.15	69.32	77.72	76.31	76.26	75.69	76.58	74.61	62.62	92.94
15.54	-	-	-	-	-	-	-	-	-	-	-	-	-	1.12
Preliminary Clay Filtration		x	x	x			x	x	x					

(a) May be taken as approximately equivalent to weight percent.
(b) Contain traces of both low and high boiling impurities, see Figures 3 and 4.

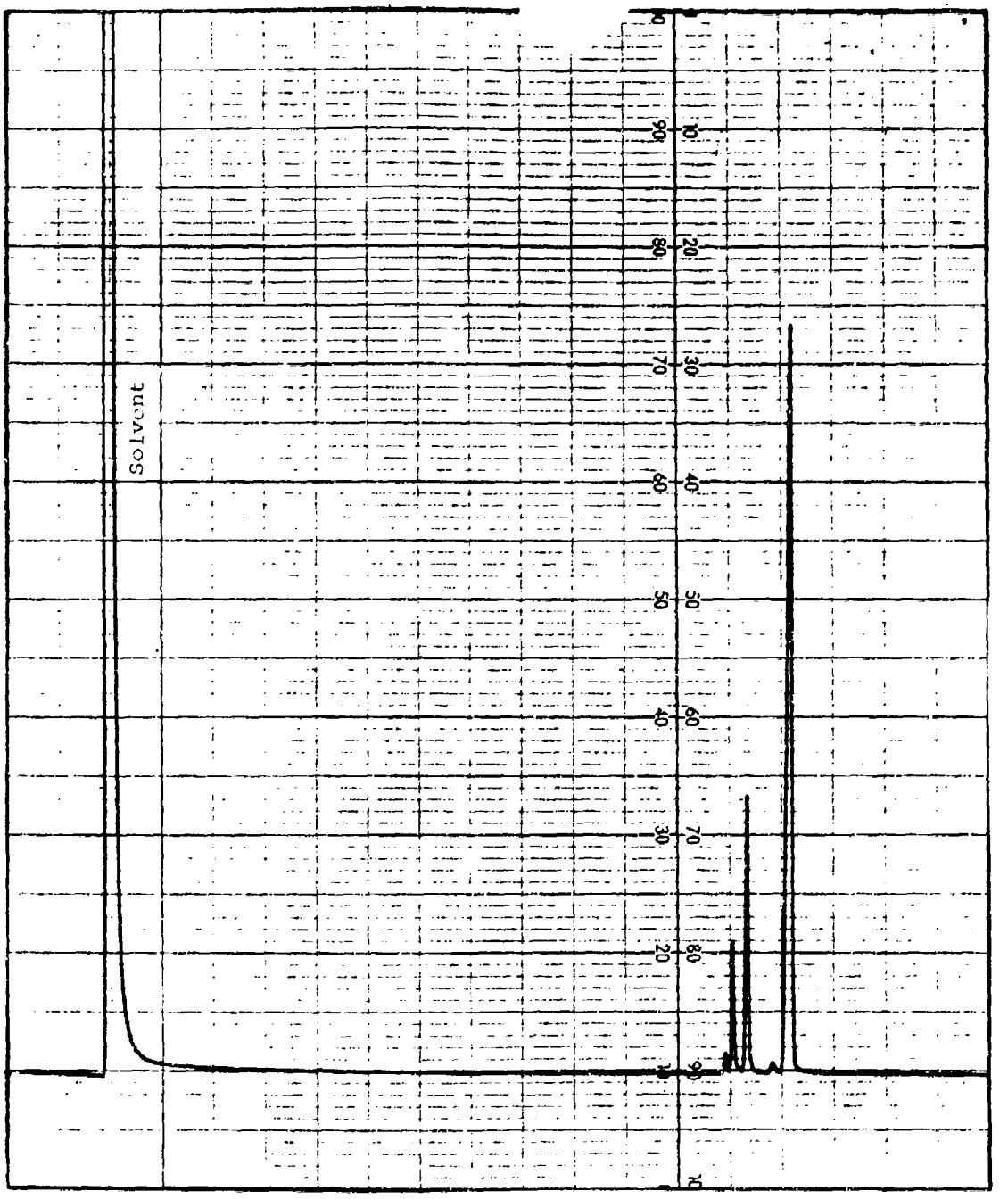

Figure 2. Gas chromatogram of fuel TMC-3.

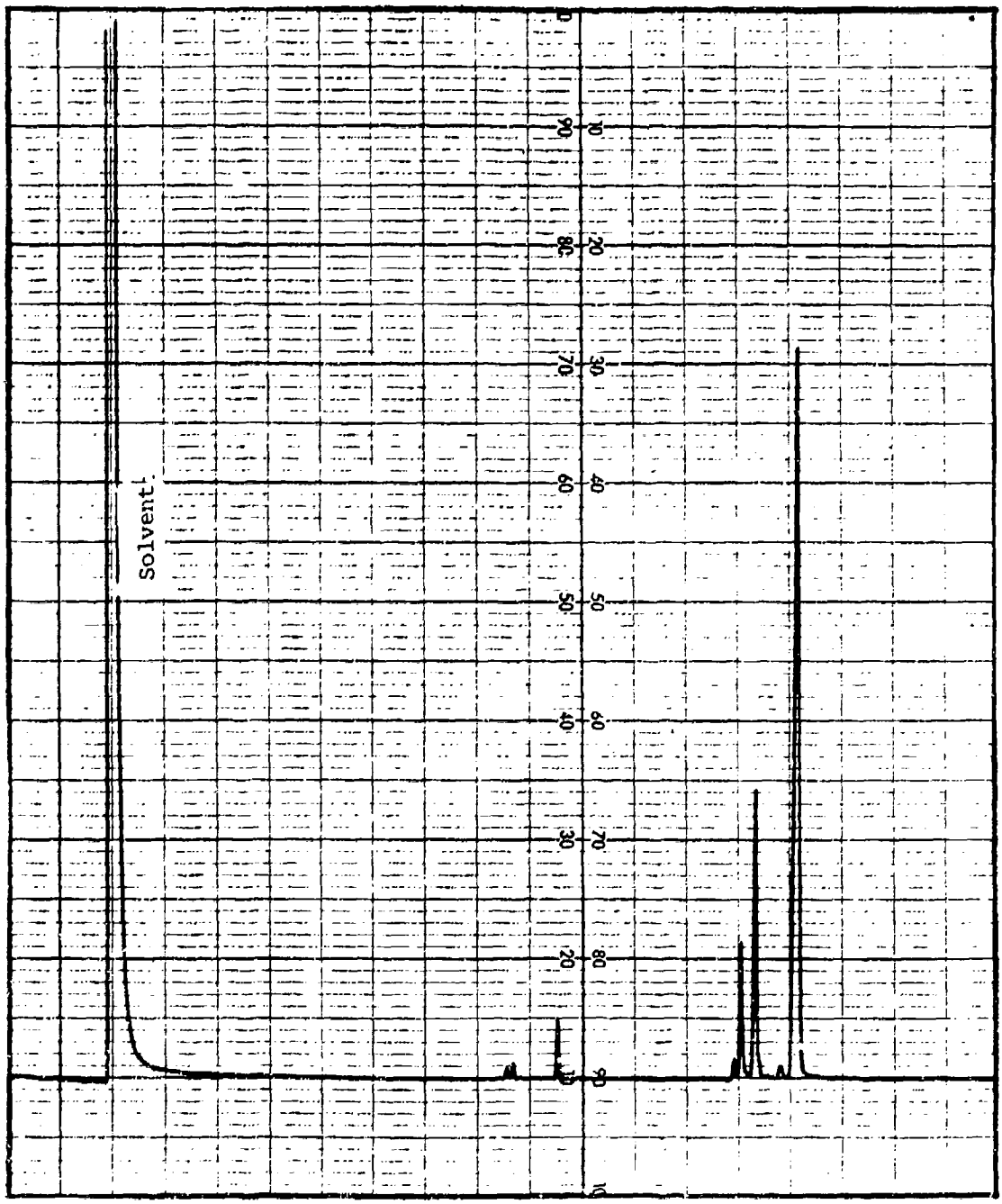

Figure 3. Gas chromatogram of fuel TMC-4.

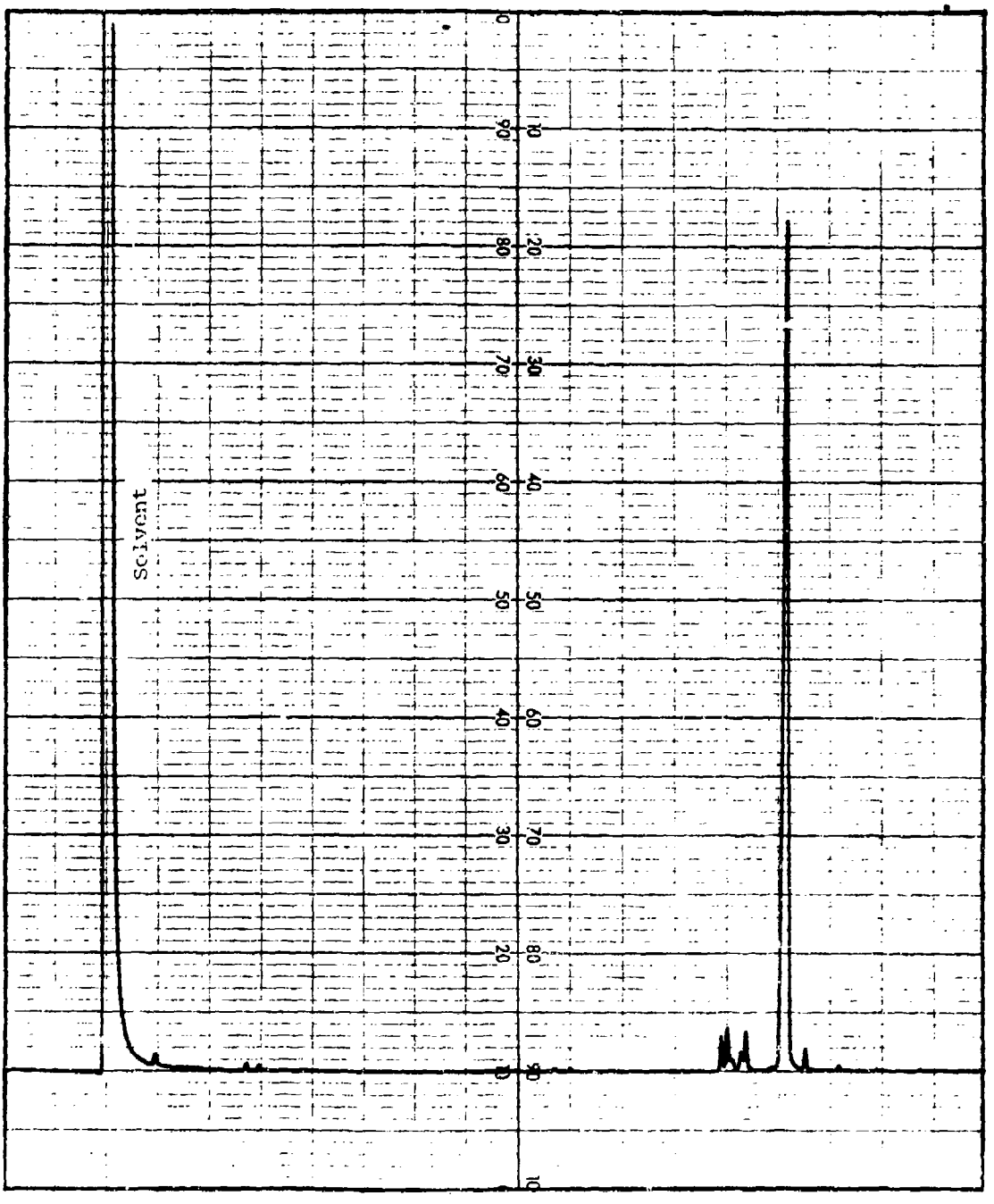

Figure 4. Gas chromatogram of fuel 7186-5 (RJ-5G).

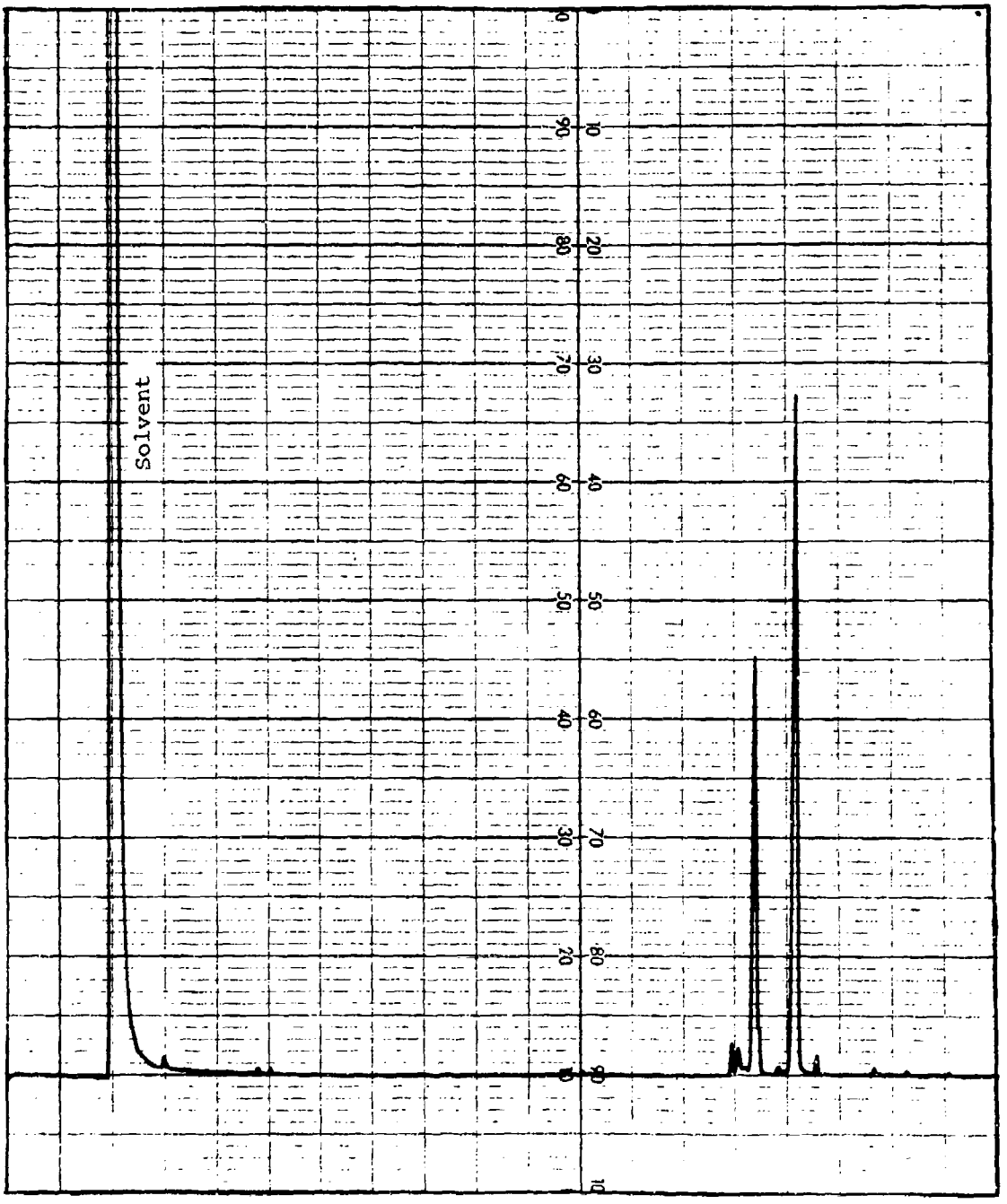

Figure 5. Gas chromatogram of fuel 7186-4 (RJ-5F, Suntech Inc)

Freeze-Point Determinations

Freezing points of the fuels were determined by freezing the sample, into which a chromel-alumel thermocouple had been immersed, with liquid nitrogen. By slowly warming the specimen, the precise melt temperature was measured. Two pure compounds, hexane and toluene, were measured in a similar way to estimate the accuracy of the procedure. Values determined for these materials showed good agreement with literature values. All freezing point data are presented in Table 24.

Kinematic Viscosity

Kinematic viscosity was determined at three temperatures between -65°F and 70°F. All fuels developed a distinct hazy appearance when cooled to -65°F. Viscosity values are presented in Table 25. ASTM viscosity charts for the samples are presented in Appendix A.

5. COMPOSITION AND PROPERTY MEASUREMENTS ON FIVE RJ-5 HIGH DENSITY FUELS

Five RJ-5 high-density fuel specimens were analyzed by gas chromatography to determine their isomeric composition and impurities. Additionally, melting points, kinematic viscosities, specific gravity, and heat of combustion were determined for the fuels.

The gas chromatographic analyses were conducted on a Perkin-Elmer Model 3920 using a 50-meter SF-96 glass capillary column. Instrument conditions are given in A of Appendix B. Area percents were calculated and were assumed to be approximately equivalent to the weight percent of components in the original fuel. Typical chromatographs are presented in Figures 6 and 7 and all data are tabulated in Table 26.

TABLE 24. MEASURED FREEZING POINT OF RJ-5 FUELS

Fuel	Temperature, °C	
TMC-1	-74	
TMC-2	-71	
TMC-3	-74	
TMC-4	-76	
TMC-5	-74	
TMC-6	-74	
TMC-7	-74	
TMC-8	-71	
TMC-9	-74	
7186-1	-71	
7186-2	-68	
7186-3	-74	
7186-4	-74	
7186-5	-72	
Toluene	-93	(literature*, -95)
Hexane	-90	(literature*, -94

*Handbook of Chemistry and Physics, 46th Ed. The Chemical Rubber Co.

TABLE 25. KINEMATIC VISCOSITY OF RJ-5 FUELS

	Centistokes		
Sample	-65°F	0°F	+77°F
TMC-1	15,700	231	21.7
TMC-2	15,200	228	21.7
TMC-3	14,300	220	21.2
TMC-4	11,500	200	20.2
TMC-5	14,870	116	14.3
TMC-6	14,700	220	21.0
TMC-7	13,400	213	20.8
TMC-8	12,900	207	20.5
TMC-9	12,700	207	20.4
7186-1	19,000	251	22.6
7186-2	17,600	238	22.0
7186-3	18,400	249	22.5
7186-4	10,600	168	17.2
7186-5	11,200	188	19.2

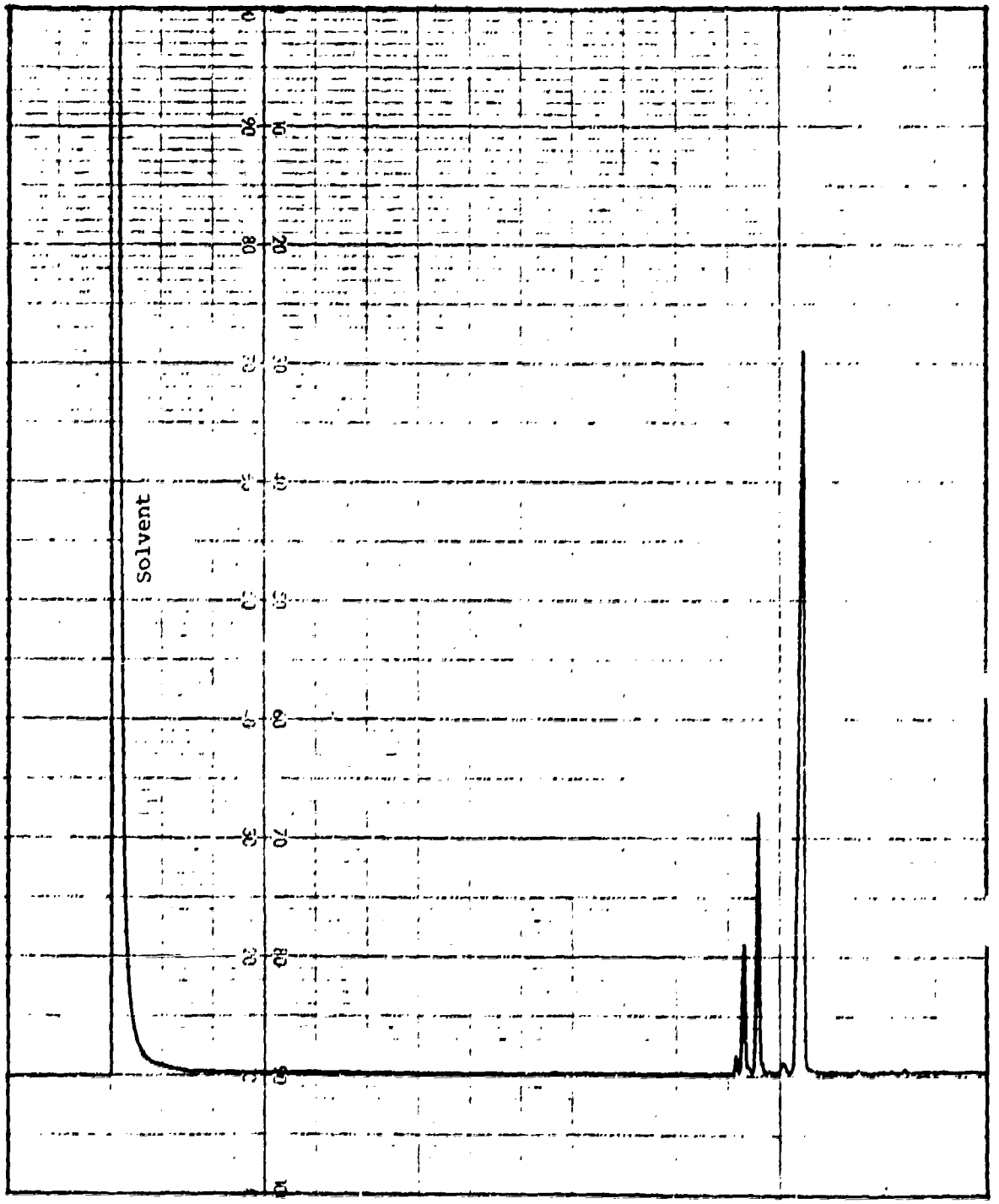

Figure 6. Gas chromatogram of RJ-5 fuel 7242-32.

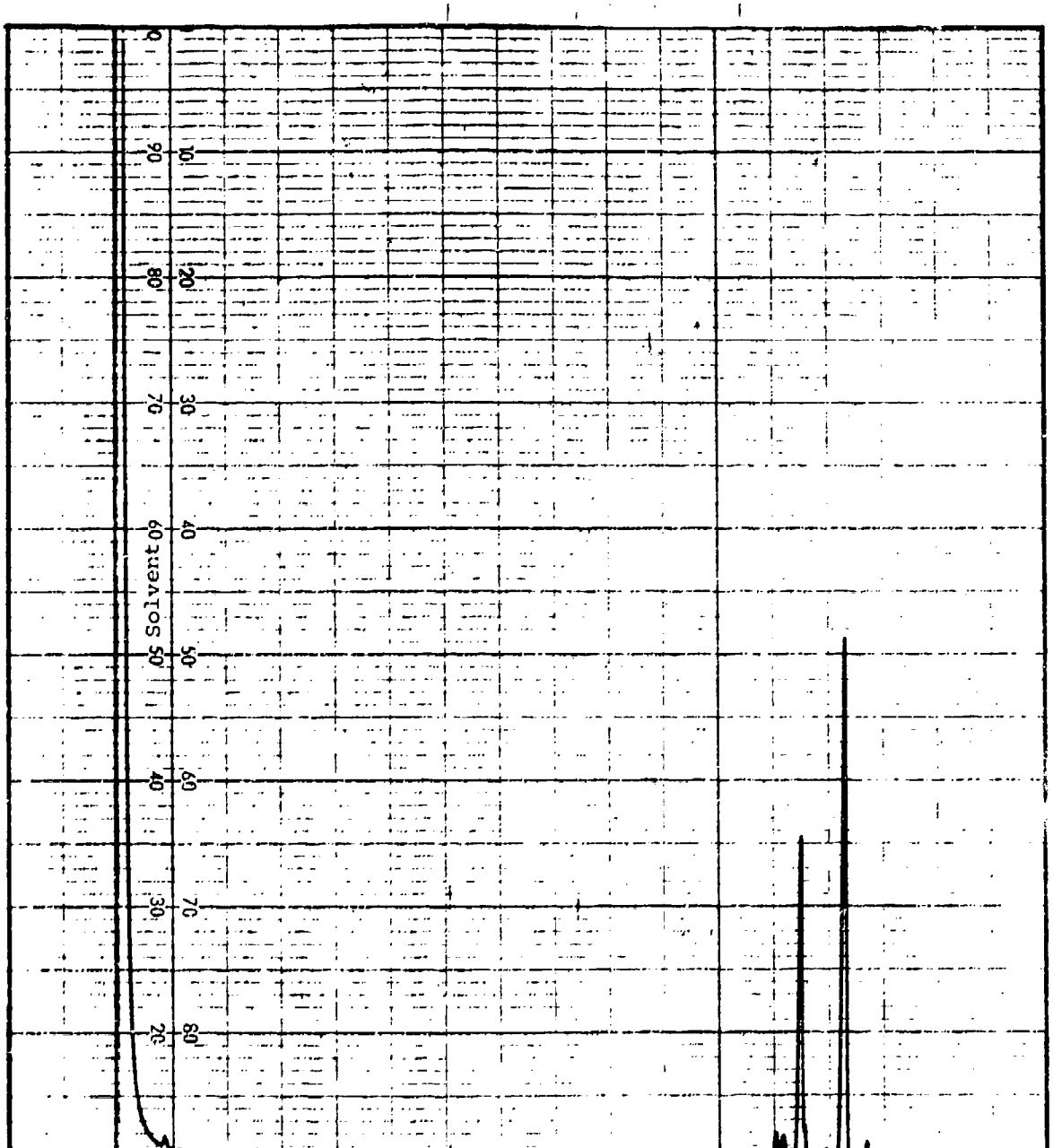

Figure 7. Gas chromatogram of RJ-5 fuel 7242-35.

TABLE 26. GAS CHROMATOGRAPHIC DATA FOR RJ-5 FUELS

Retention Time (Min)	Area Percents*				
	7242-32	7242-33	7242-34	7242-35	7242-36
4.66	-	-	-	0.44	-
4.89	-	-	-	0.42	-
14.14	0.90	0.95	0.91	1.67	0.57
14.26	7.36	7.32	6.90	1.57	15.76
14.59	15.58	15.55	15.68	31.96	18.28
14.65	-	-	-	1.49	-
15.05	1.00	1.05	1.10	-	1.19
15.45	75.17	75.14	75.40	61.45	64.20
15.78	-	-	-	0.99	-

*May be taken as approximately equivalent to weight percent.

Melting points were determined for the fuels by gradually warming the fuel after its solidification in liquid nitrogen. Temperatures were measured by a thermocouple contained in the frozen fuel. Melt data are presented in Table 27.

Kinematic viscosity was determined at three temperatures: -65°F, 0°F and 70°F. One fuel (no. 7242-36), though not frozen at -65°F, became completely immobile at that temperature and a meaningful viscosity value could not be obtained. Viscosity data are presented in Table 28.

Heat of combustion values (ASTM D240) are presented in Table 29. Specific gravities at 25°C (77°F) are presented in Table 30.

6. DETERMINATION OF SPECIFIC TRACE ELEMENTS IN JP-9 FUELS

The combustion products of certain JP-9 fuels were reported to cause pitting and erosion of MAR M509 metal, an alloy of chromium and cobalt. The corrosive nature of the combustion gases were suspected to be related to impurities in the fuels. Analyses were conducted on a series of fuels to determine the presence and concentration of catalyst materials which may have been introduced during the synthesis of fuel components. Ten fuels were examined for the presence of iron, zinc, aluminum, chlorine and phosphorus.

Iron, Zinc and Aluminum Analyses

The three metals were measured in the fuels by atomic absorption spectrophotometry. Each fuel was diluted with methylisobutylketone (MIBK) which, for the zinc and aluminum analyses, was then aspirated directly into the flame. An air-acetylene flame was employed for zinc; and nitrous oxide-acetylene was used for aluminum. A carbon rod atomizer was used in the iron analysis.

TABLE 27. MELT POINT DATA FOR RJ-5 FUELS

Sample	Temperature, °C
7242-32	-73
7242-33	-72
7242-34	-78
7242-35	-73
7242-36	-71
Toluene Reference	-96 (literature, -93)

TABLE 28. KINEMATIC VISCOSITY OF RJ-5 FUELS

	Centistokes		
Sample	-65°F	0°F	+77°F
7242-32	18,900	249	22.6
7242-33	19,100	251	22.6
7242-34	15,200	226	21.6
7242-35	10,800	170	17.2
7242-36	-*	222	20.3

*Value not obtained because fuel, though not frozen, became completely immobile at this temperature.

TABLE 29. HEAT OF COMBUSTION OF RJ-5 FUELS

Sample Code	Gross, BTU/lb		Net, BTU/lb
7242-32	18,778		
	18,731		
	Average	18,754	17,846
7242-33	18,727		
	18,775		
	Average	18,751	17,843
7242-34	18,774		
	18,789		
	Average	18,782	17,873
7242-35	18,752		
	18,748		
	Average	18,750	17,842
7242-36	18,738		
	18,756		
	Average	18,747	17,839

TABLE 30. SPECIFIC GRAVITY OF RJ-5 FUELS

Sample Code	77°F/77°F
7242-32	1.0791
7242-33	1.0798
7242-34	1.0793
7242-35	1.0725
7242-36	1.0714

Standards were prepared from organo-metal reference compounds. The procedure is one commonly employed for the analysis of metals in hydrocarbon mixtures (5). Good sensitivity was obtained for iron and zinc. However, the minimum detection limit for aluminum was only approximately 25 ppm. The aluminum concentration was found to be less than that for all samples. Both aluminum and chlorine analyses are intended to signal the potential presence of an aluminum chloride catalyst carryover. Weight and atomic ratios, however, favor the use of chlorine as an indicator for $AlCl_3$. High sensitivity is thus less important for aluminum than for the other metals. The values for zinc and iron are presented in Table 31. No aluminum was detected.

Iron acetylacetonate, a catalyst employed in RJ-5 synthesis, has been shown by experiments to be quantitatively removed from JP-9 by extraction with hydrochloric acid. Acid extractions were applied to several of the fuel samples. As confirming analyses, extracted iron was measured by atomic absorption using aqueous iron standards. These determinations, given in Table 31, agree well with values obtained by previous direct measurements on fuels.

Phosphorus Determination

Phosphorus contamination in the fuels could potentially arise from the use of triphenylphosphine as a catalyst for synthesis. The fuels were examined for organo-phosphorus compounds by gas chromatography using a phosphorus-nitrogen detector (Bodenseewerk Perkin Elmer & Co. GMBH) operating in the phosphorus mode. This detector depends upon a thermionic reaction which results in the release of negative ions to detect nitrogen or phosphorus compounds. The unit is made completely specific for phosphorus compounds by adjusting the hydrogen flow so that nitrogen compounds are fully burned in the flame. The detector is grounded

in such a way that electrons produced in the normal combustion process cause no response.

The detector was installed in a Perkin-Elmer Model 3920 gas chromatograph with an 18" x 1/8" stainless steel column packed with 5% SE-30 on chromosorb W-HP. The column was operated at 210°C. Under these conditions normal fuel components elute quickly causing only a small deflection in the base-line. Two phosphorus compounds, triphenylphosphine and triphenylphosphine oxide, were detected in most of the fuels. In all cases, triphenylphosphine was present at a much higher level than the oxide. A typical chromatograph for these components in a fuel is presented in Figure 8. Standards for these compounds were prepared in phosphorus-free JP-9. In cases where these compounds were found to exceed 50 ppm in the fuel, samples were diluted 10-fold with heptane. A value for total phosphorus was calculated from the measured amount of each of the two phosphorus compounds. Total phosphorus values determined in this manner are included in Table 31.

Any phosphorus-containing material that can be chromatographed will be detected by this technique. A conventional elemental analysis for total phosphorus was not possible for most of the samples because of the small amount of sample available and the low level of phosphorus.

Chlorine Determination

Chlorine was determined by burning a portion of each fuel in an oxygen bomb. Hydrogen chloride generated during the combustion was reacted with an aliquot of 0.2N sodium carbonate solution. The chloride content of the solution was then measured using an Orion Model 97-17 solid-state chloride-ion electrode. Calibration was achieved by the method of standard additions.

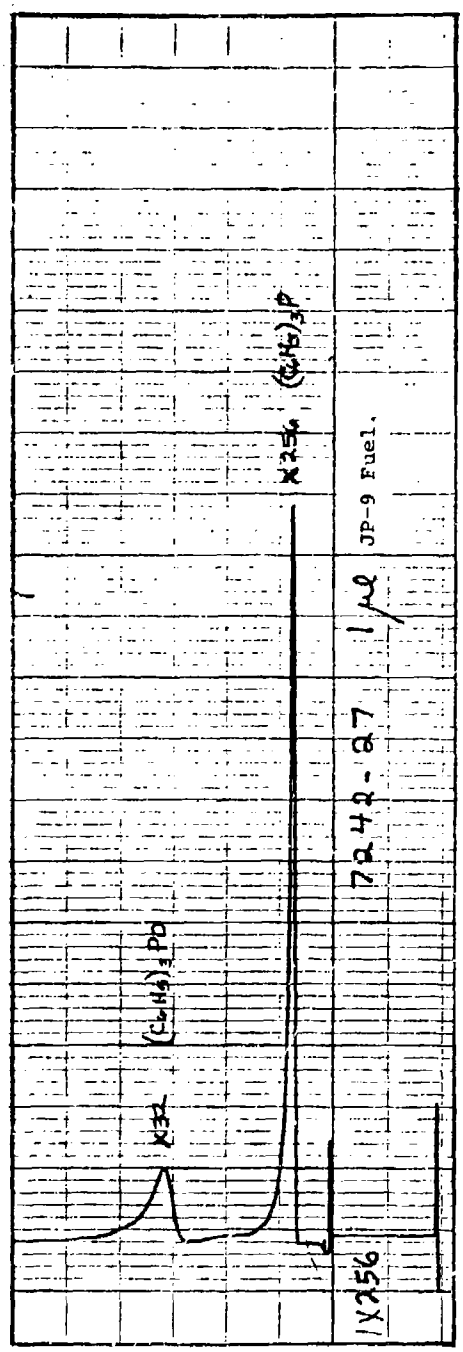

Figure 8. Gas chromatogram of phosphorus compounds in JP-9 7242-27 using a phosphorus-specific detector.

TABLE 31. ANALYSIS OF SELECTED TRACE ELEMENTS IN JP-9 FUELS

Sample	Concentration, ppm (wt)				
	Iron Direct Method	Iron Extraction Method	Zinc	Phosphorus[a]	Chlorine
7242-21	0.13	0.2	1.6	1	<5
7242-22	0.09	0.1	3.3	N.D.[c]	<5
7242-23	0.10	-[b]	3.0	38	950
			(Replicate determination)		972
7242-24	1.7	1.7	<1	22	<5
7242-25	0.09	-	3.3	53	<5
7242-26	0.15	-	2.2	1	<5
7242-27	0.05	-	1.0	1	<5
7242-28	0.06	<0.1	1.9	111	<5
7242-29	0.08	<0.1	2.1	63	<5
7242-30	0.17	-	<1.0	2	<5
7242-31	0.15	-	1.0	1082[d]	<5

(a) Calculated from measured concentrations of triphenylphosphine and triphenylphosphine oxide.

(b) Dash indicates sample not analyzed.

(c) N.D. = none detected.

(d) Sample spiked with approximately 1,000 ppm phosphorus as $(C_6H_5)_3P$.

The detection limit for chlorine in the fuel by this method was approximately 5 ppm. A signficant amount of chlorine was detected only in one fuel, No. 7242-23.

7. CHARACTERIZATION OF BLENDS OF JP-10 AND MONOISOMERIC RJ-5

In order to characterize a series of high-density fuels consisting of blends of RJ-5G and JP-10, gas chromatographic analyses were conducted; heat of combustion, kinematic viscosity as a function of temperature, and specific gravity were determined.

A Perkin-Elmer Model 3920-B gas chromatograph was used for the analysis. Instrument conditions conformed to those in A of Appendix B. In order to convert integrated peak area percent to weight percent, a response factor was calculated for RJ-5G relative to JP-10. Data are presented in Table 32. Chromatograms are presented in Figures 9-14.

Kinematic viscosity (ASTM D 445) was measured at the temperatures 77°, 0° and -65°F. Fuels were noticeably cloudy at -65°F and showed a tendency to form solid particles. Data are plotted on ASTM standard viscosity-temperature charts as shown in Figures 15-20. It is interesting to note that the viscosity plots have a slight curvature for fuel in which JP-10 is the most abundant component. Fuels having 40% (wt) or less JP-10 give linear ASTM temperature-viscosity plots. Viscosity values are presented in Table 33.

Heat of combustion was determined for each fuel blend. Net values were calculated using the gross heat of combustion and the hydrogen content computed using the nominal composition of each sample and the theoretical value for the individual constituents. Values are presented in Table 34.

TABLE 32. GAS CHROMATOGRAPHIC DATA

Retention time, min	Weight, Percent*					
	7263-43	7263-44	7263-45	7263-46	7263-47	7263-48
2.93	-	0.61	0.26	0.18	-	0.85
4.63	-	0.28	0.15	0.11	-	0.45
4.87	-	0.23	-	-	-	0.42
6.99	99.00	18.49	39.35	59.24	79.90	-
7.31	0.19	-	-	-	0.16	-
7.48	0.81	0.21	0.36	0.53	0.67	-
Total JP-10	100.00	18.70	39.71	59.77	80.73	-
12.40	-	0.83	-	-	-	-
14.13	-	1.51	1.10	0.72	0.38	1.91
14.25	-	2.54	1.22	0.81	0.42	3.20
14.62	-	1.99	1.57	1.04	0.53	2.49
15.47	-	71.69	55.11	36.85	17.73	89.52
15.78	-	1.61	0.88	0.57	0.21	1.16
Total RJ-5G	-	79.34	59.88	39.99	19.27	98.28

*Correction applied for the difference in detector response to RJ-5G and JP-10.

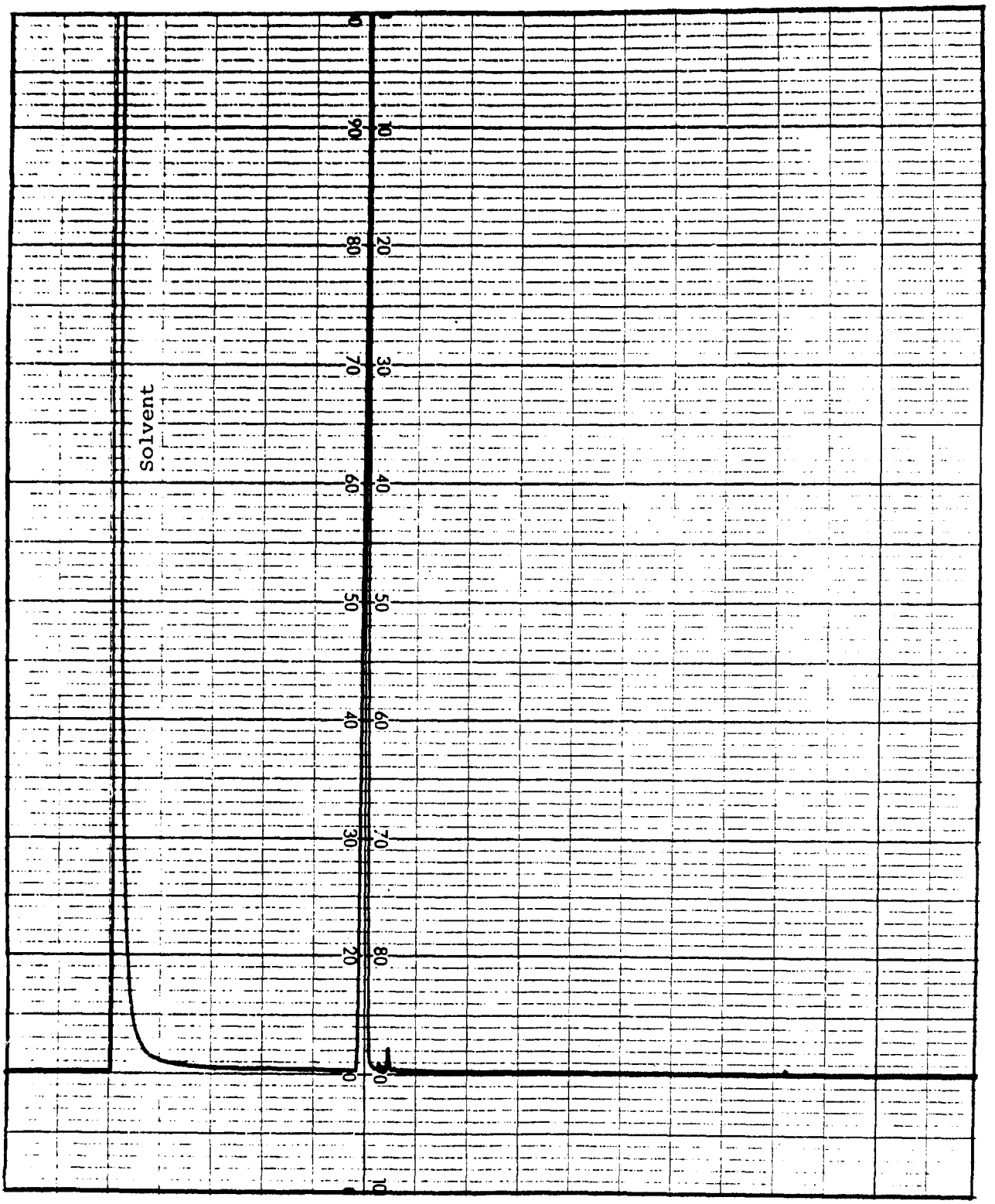

Figure 9. Gas chromatogram of fuel 7263-43, JP-10.

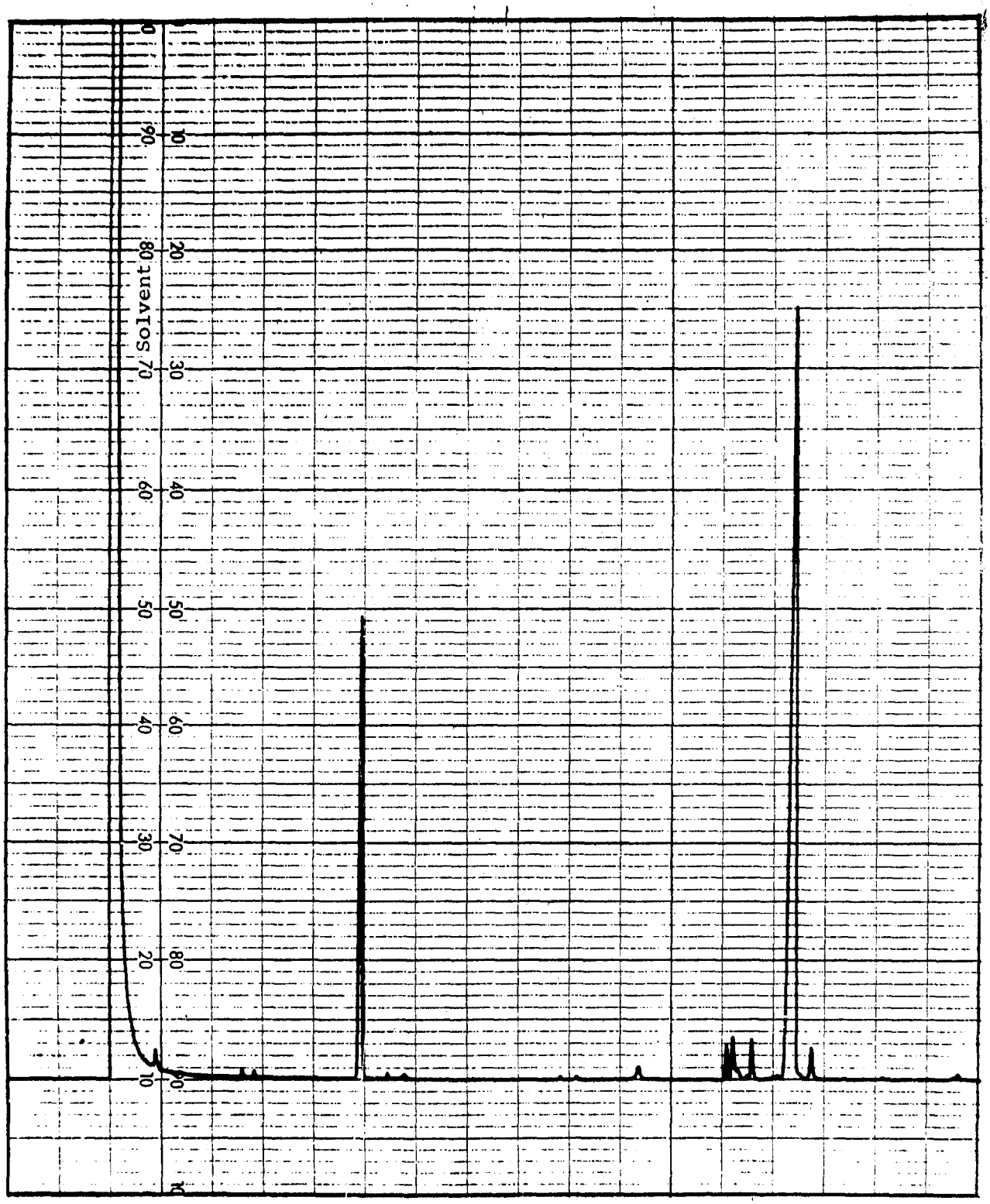

Figure 10. Gas chromatogram of fuel 7263-44.

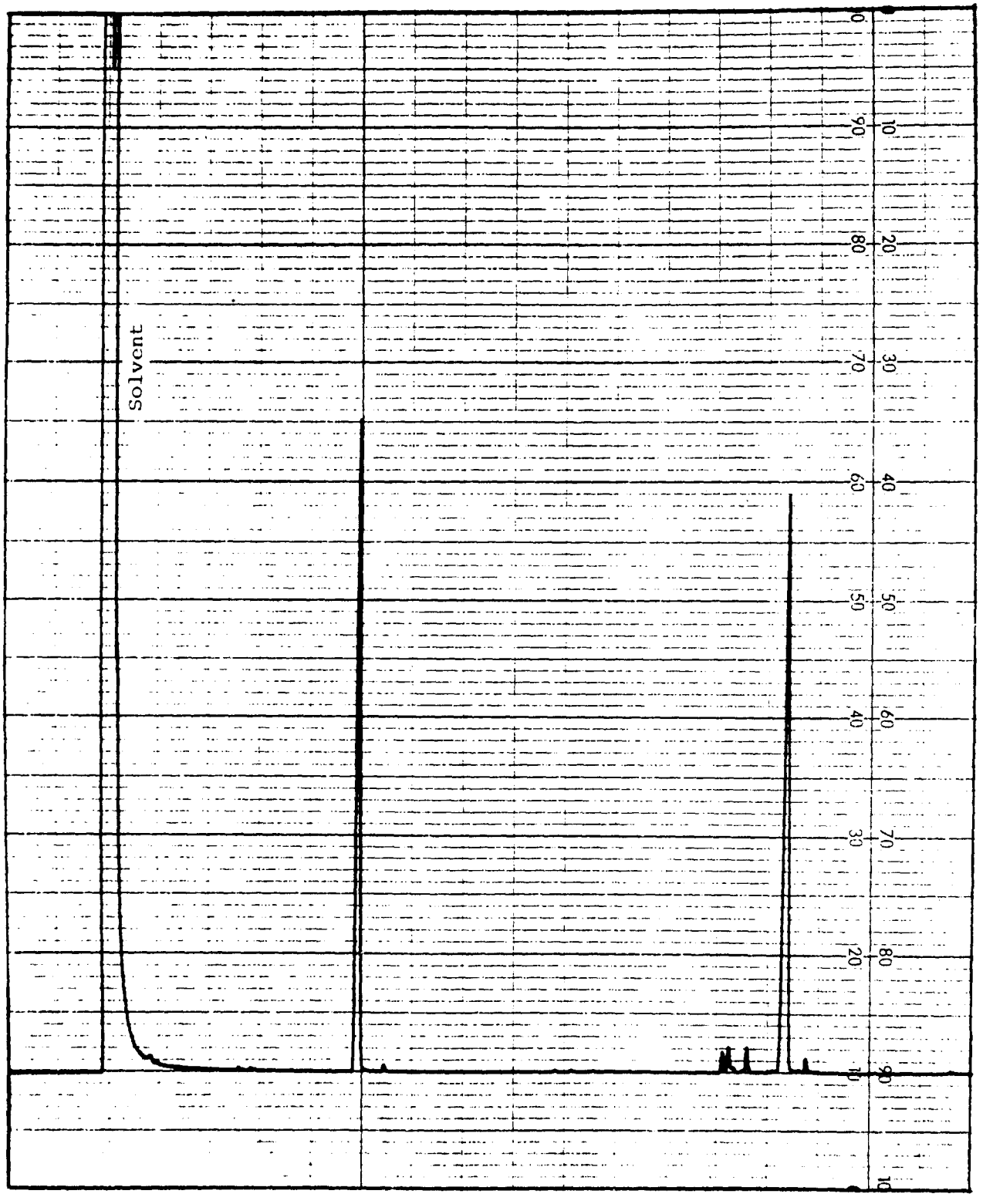

Figure 11. Gas chromatogram of fuel 7263-45.

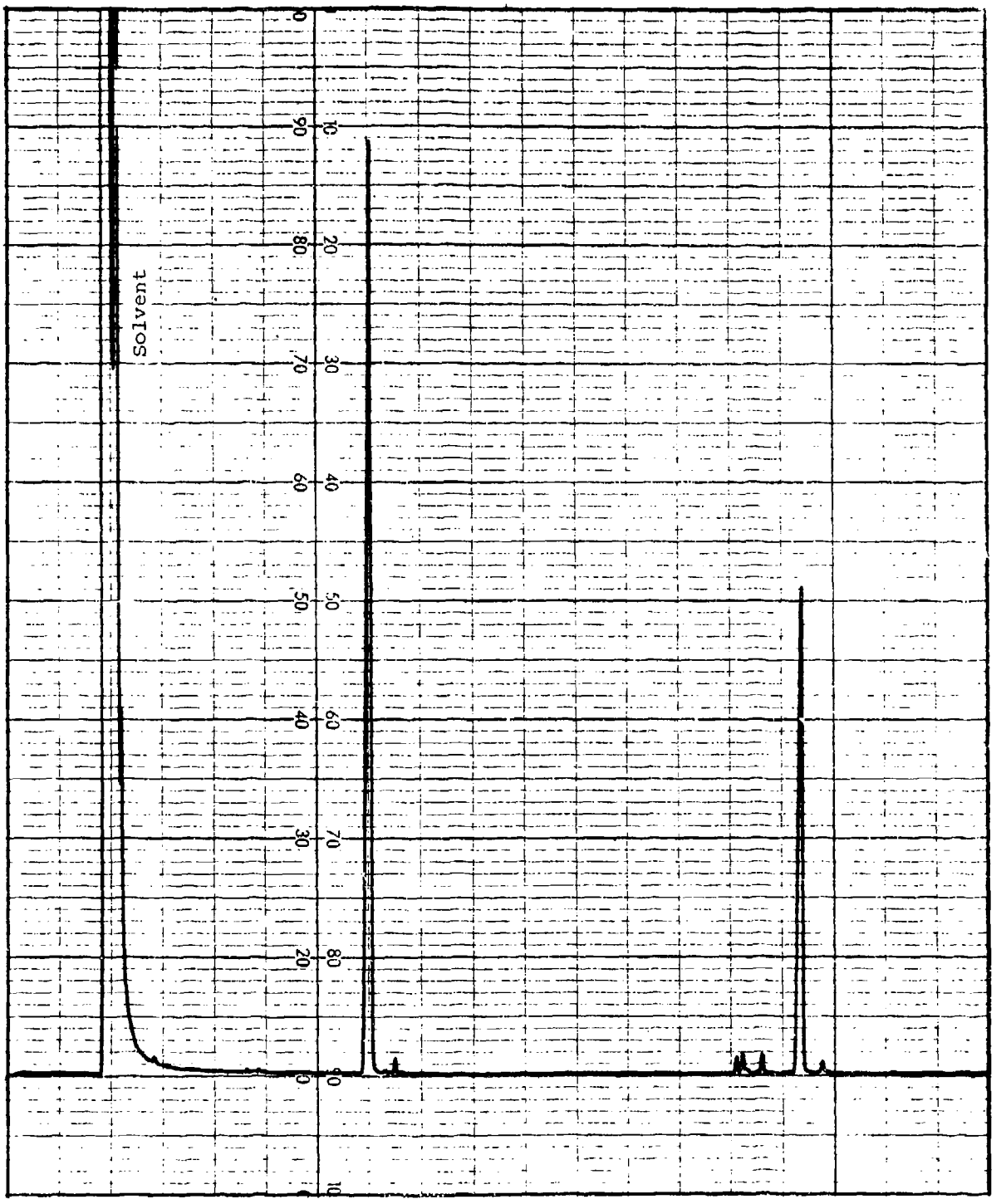

Figure 12. Gas chromatogram of fuel 7263-46.

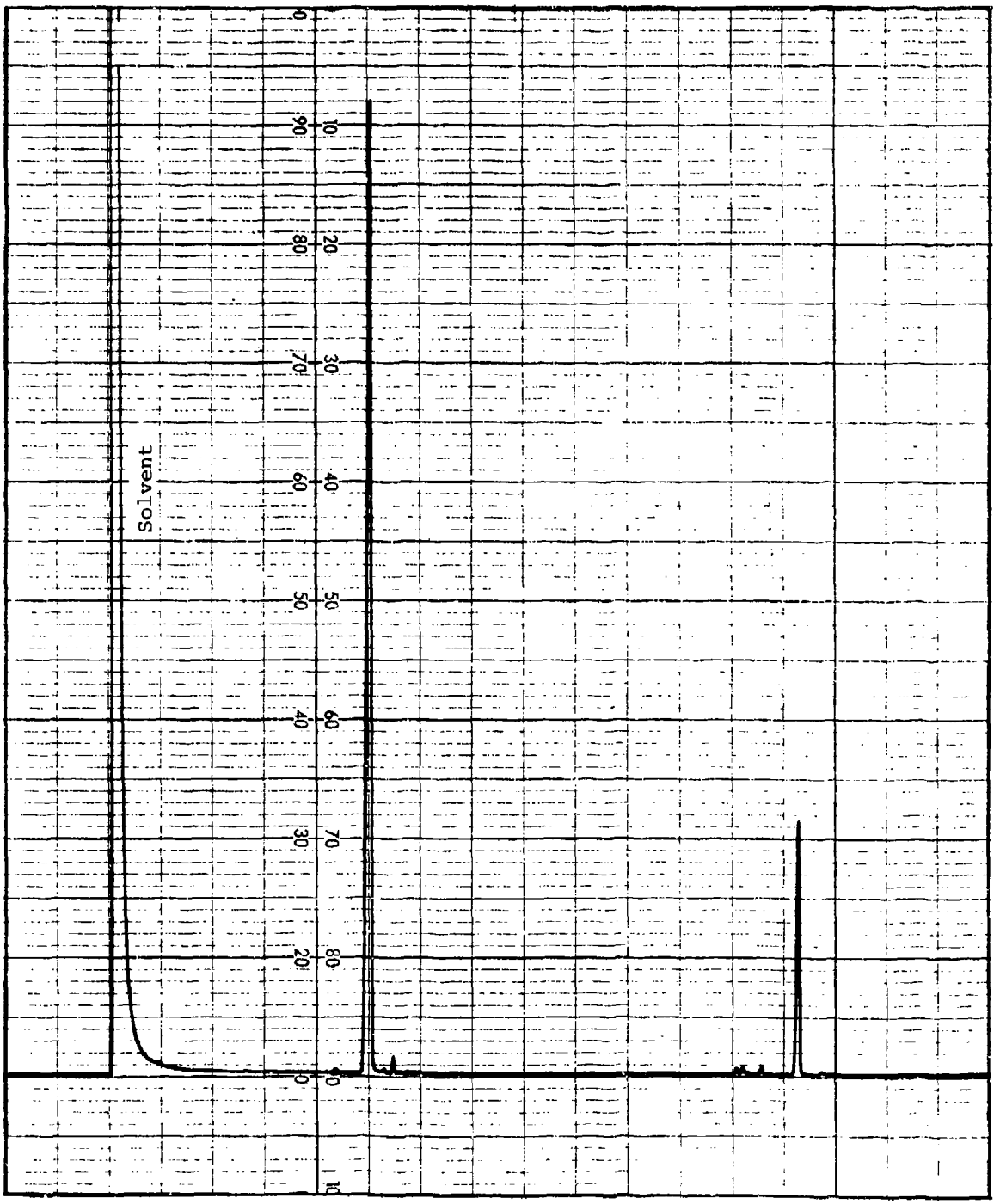

Figure 13. Gas chromatogram of fuel 7263-47.

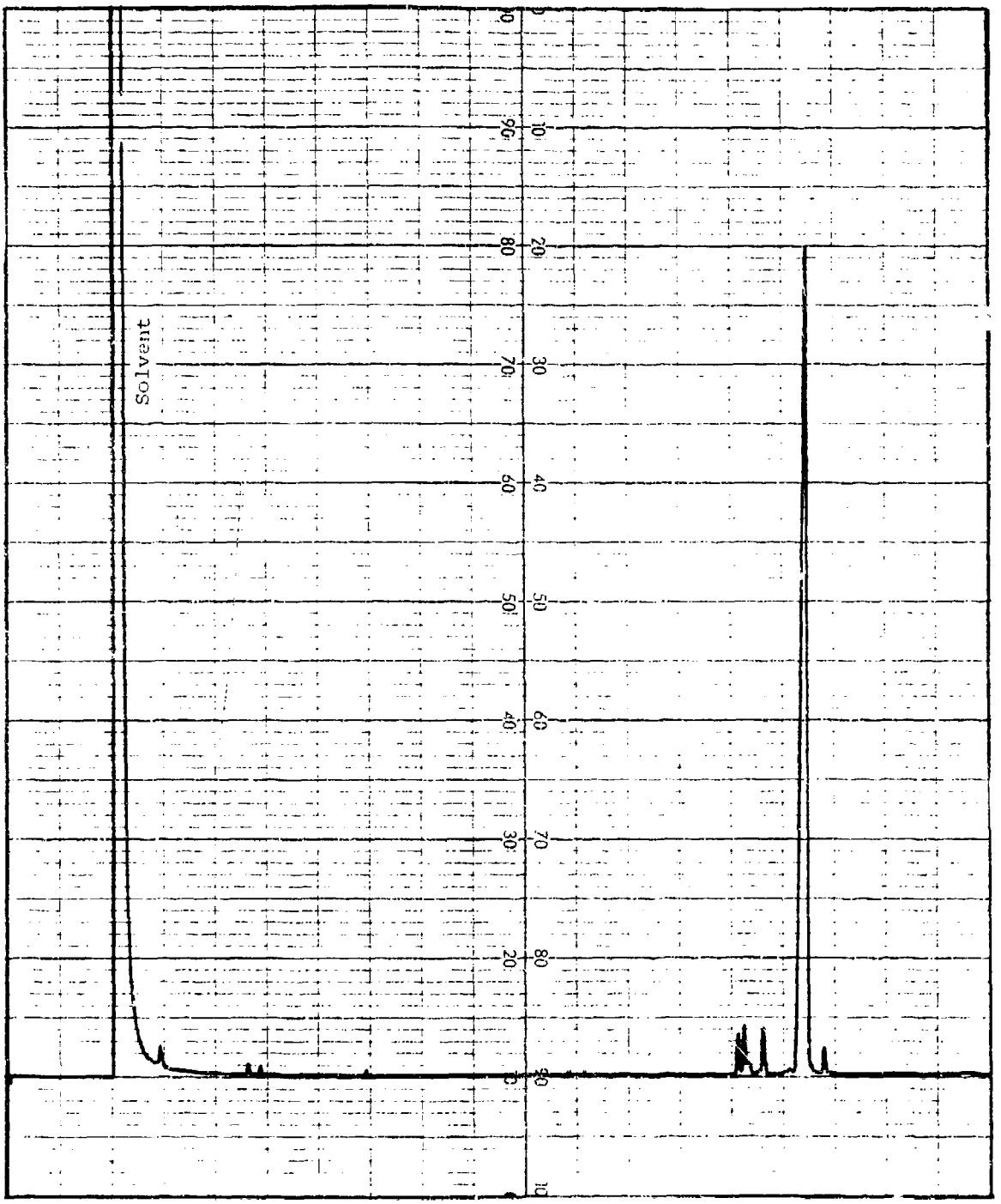

Figure 14. Gas chromatogram of fuel 7263-48.

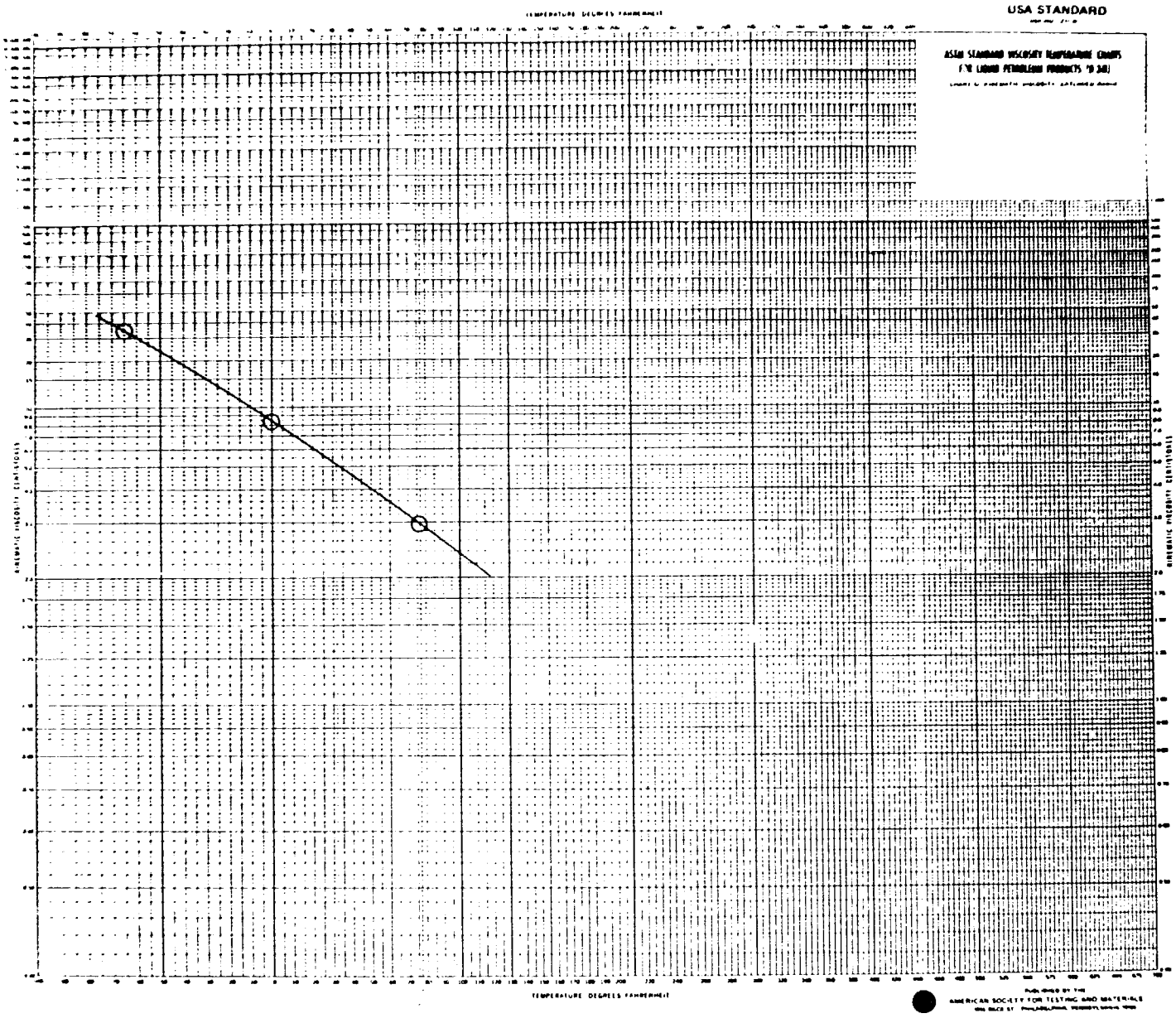

Figure 15. Fuel 7263-43, kinematic viscosity, extended range, for JP-10.

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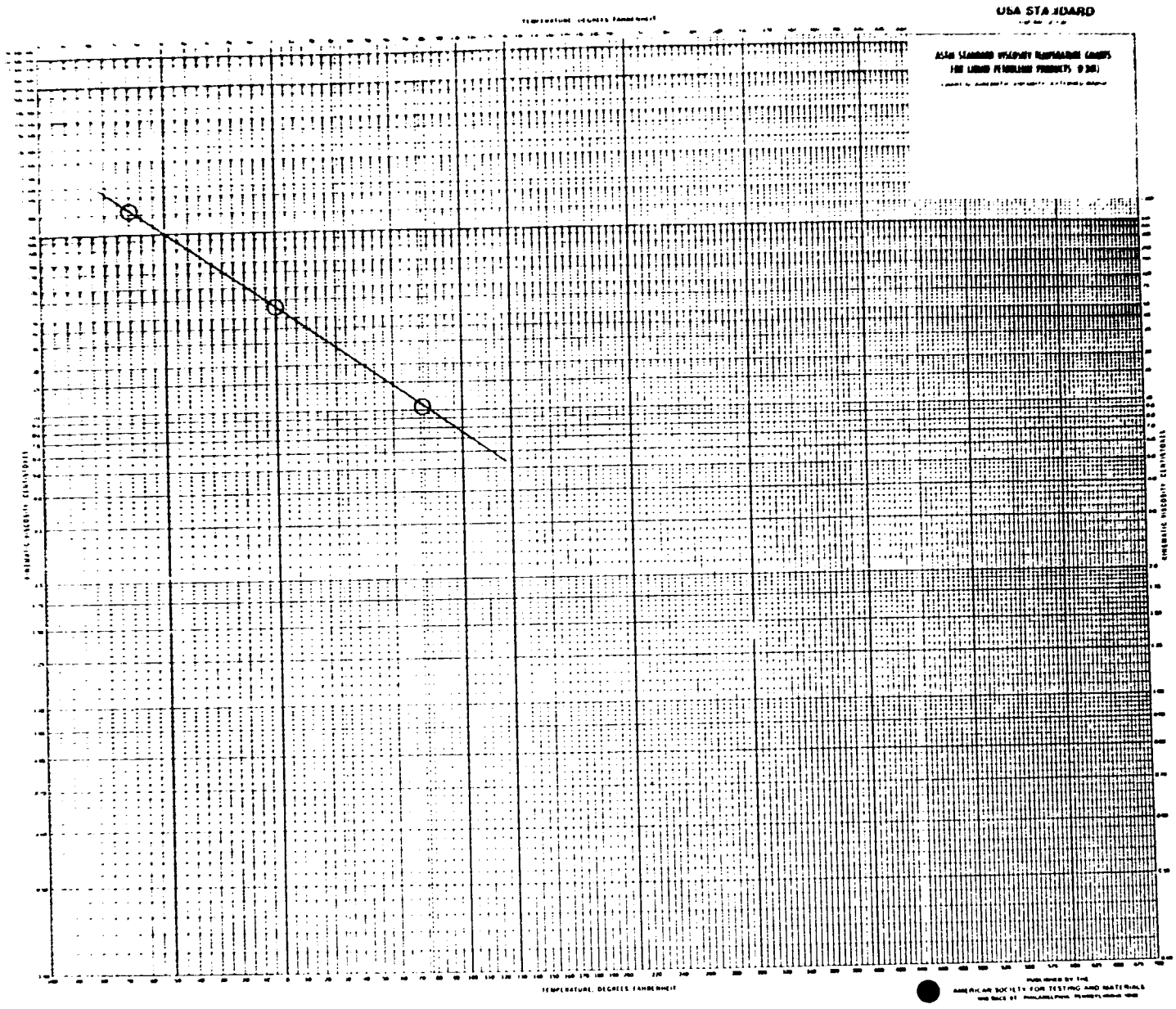

Figure 16. Fuel 7263-44, kinematic viscosity, extended range, for 20% JP-10.

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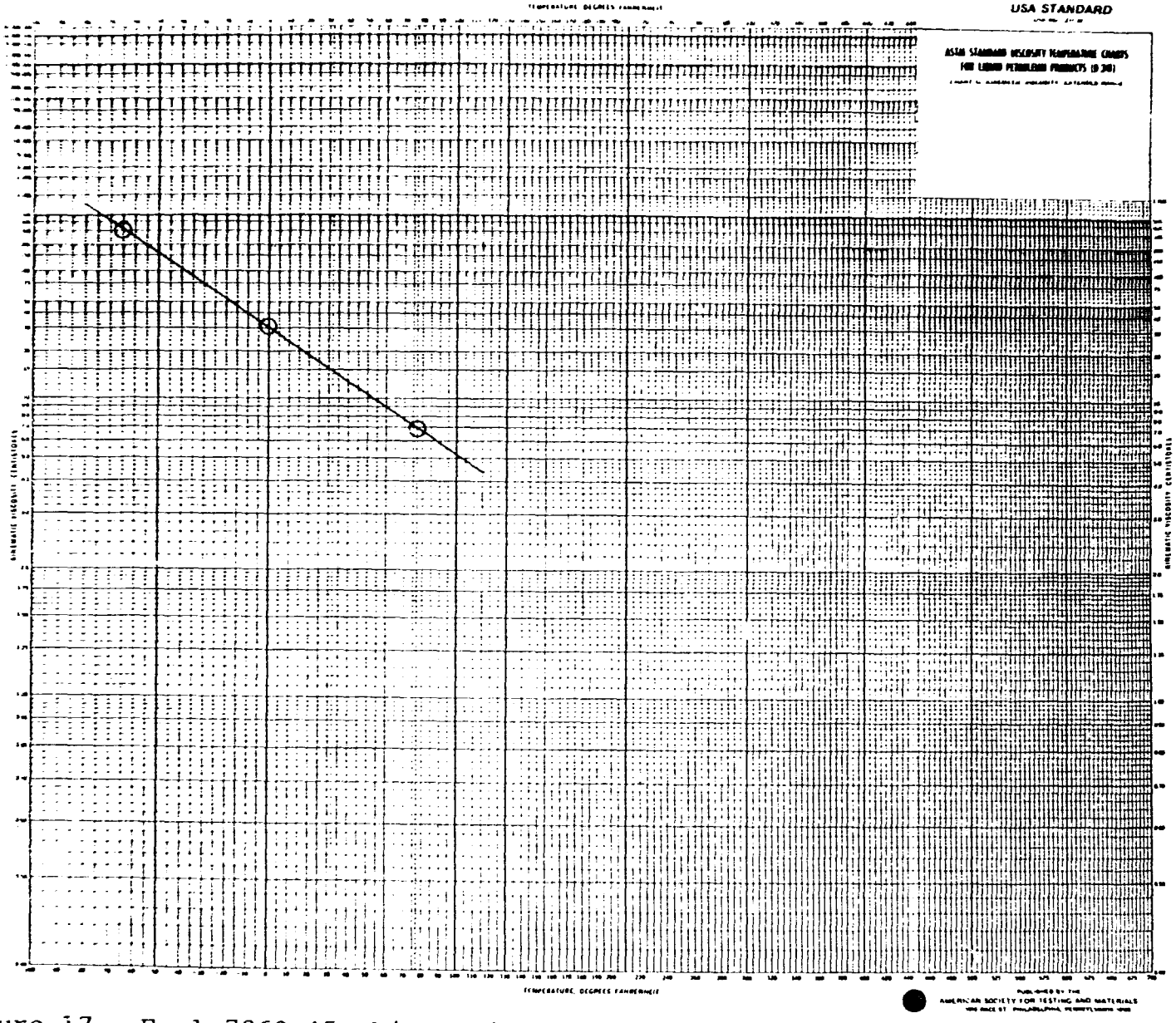

Figure 17. Fuel 7263-45, kinematic viscosity, extended range, for 40% JP-10.

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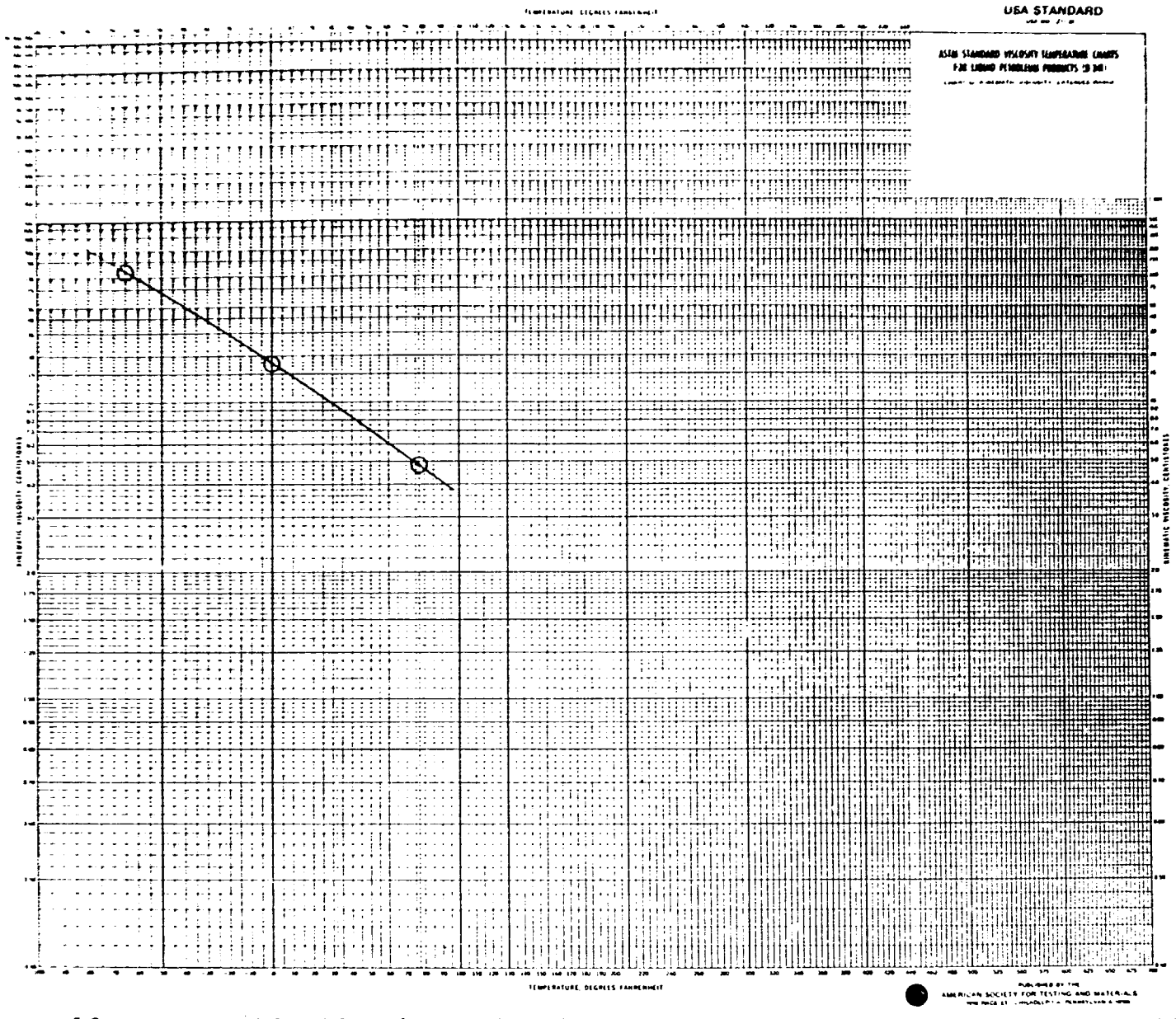

Figure 18. Fuel 7263-46, kinematic viscosity, extended range, for 60% JP-10.

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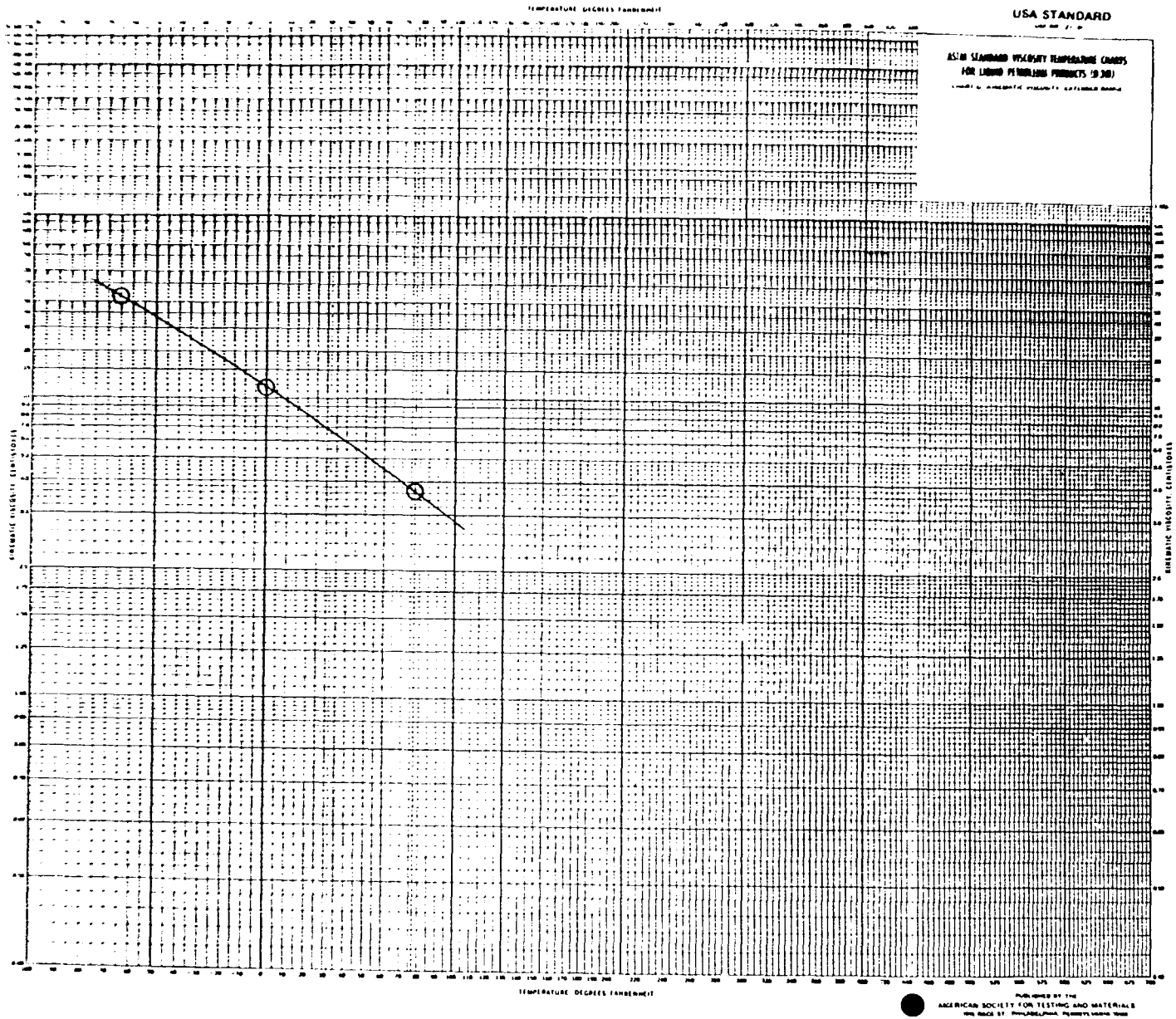

Figure 19. Fuel 7263-47, kinematic viscosity, extended range, for 80% JP-10.

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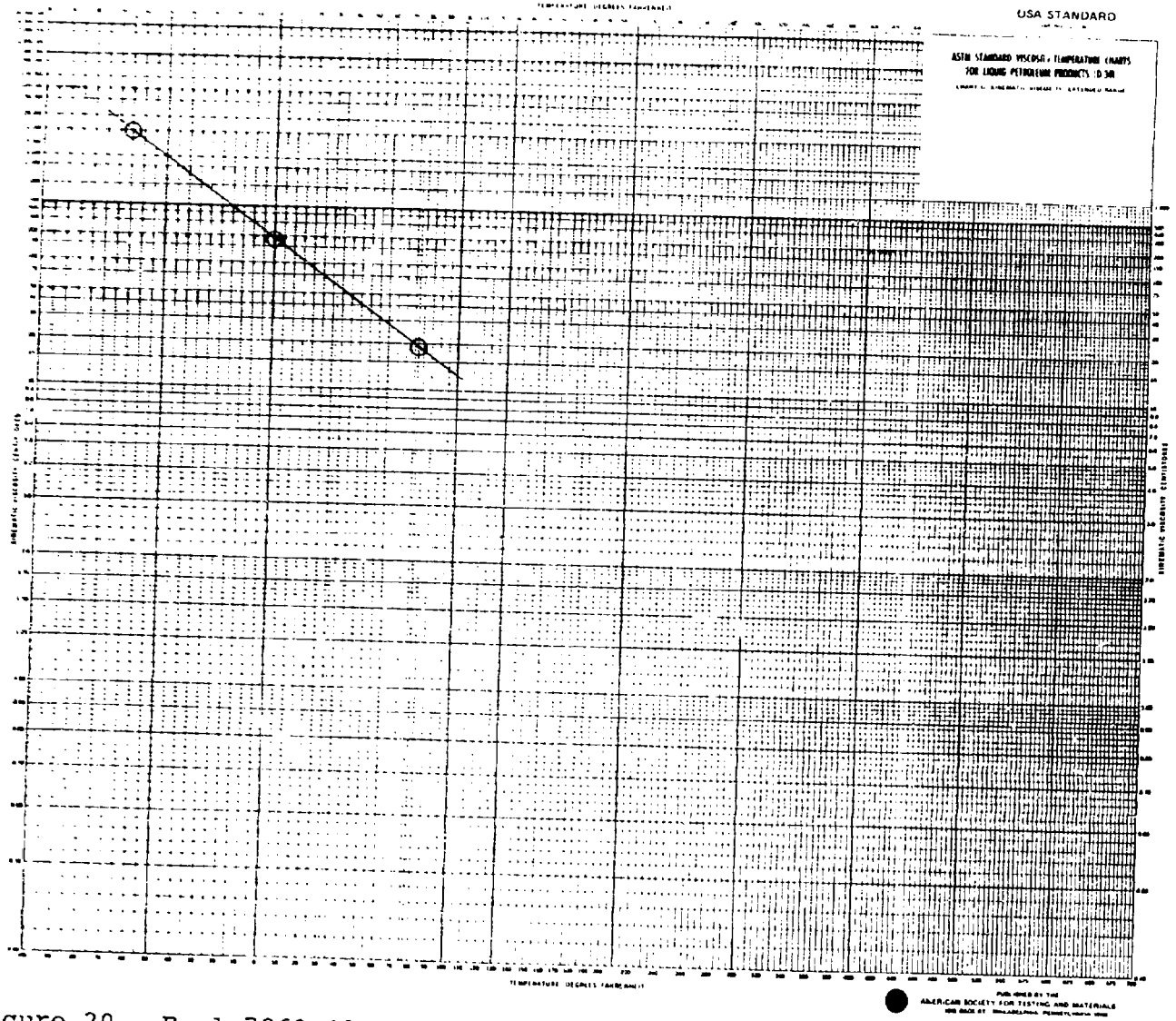

Figure 20. Fuel 7263-48, kinematic viscosity, extended range, for RJ-5G.

TABLE 33. KINEMATIC VISCOSITY OF HIGH DENSITY FUEL BLENDS

Sample	Nominal Composition	Centistokes 77°F	0°F	-65°F
7263-43	100% JP-10	2.96	8.36	34.54
7263-44	20% JP-10	10.66	63.38	1186
7263-45	40% JP-10	6.93	31.04	308.7
7263-46	60% JP-10	4.84	17.57	115.5
7263-47	80% JP-10	3.66	11.52	56.28
7263-48	100% RJ-5G	18.87	179.5	9884

TABLE 34. HEAT OF COMBUSTION

Sample	Calculated % Hydrogen*	BTU/lb Gross	Net
7263-43 JP-10	11.99	19,120 19,146	
		Av. 19,133	18,039
7263-44 20% JP-10	10.35	18,855 18,824	
		Av. 18,839	17,895
7263-45 40% JP-10	10.76	19,005 18,968	
		Av. 19,986	18,005
7263-46 60% JP-10	11.17	19,020 19,028	
		Av. 19.024	18,005
7263-47 80% JP-10	11.58	19,112 19,094	
		Av. 19,103	18,047
7263-48 RJ-5G	9.95	18,775 18,806	
		Av. 18,790	17,882

*Calculated using the hydrogen content of pure JP-10 and RJ-5; required for determination of net heat of combustion.

Specific gravities at 60°/60°F were determined by the dilatometer method and are presented in Table 35.

8. ANALYSIS AND PHYSICAL CHARACTERIZATION OF FOUR JP-9 FUELS

Four specimens of JP-9 fuels were characterized by gas chromatographic analysis and measurement of true vapor pressure, kinematic viscosity and specific gravity.

Gas chromatographic analyses were conducted using a Perkin-Elmer Model 3920-B gas chromatograph with a 50-meter glass capillary column coated with SF-96. Analytical conditions were identical to those employed on similar fuels, subsections 4, 5 and 7, and as given in A of Appendix B. Response factors were calculated and applied for JP-10 and RJ-5 relative to MCH. Chromatographic data are presented in Table 36. Vapor pressure was determined as a function of temperature using an all-glass microvapor pressure apparatus and the technique described in subsection 1. Kinematic viscosities were measured at -65°, 0° and 77°F using ASTM procedure D 445. Data plotted on ASTM viscosity-temperature charts are presented in Figures 21-23.

The specific gravity of each fuel was measured at 60°F relative to water at the same temperature. Values for vapor pressure, viscosity and specific gravity are presented in Table 37.

9. VAPOR PRESSURE OF HIGH DENSITY FUEL BLENDS

Vapor pressure as a function of temperature was determined for each of seven high density fuels and fuel blends. Blends were prepared by accurately weighing the pure individual components RJ-5G (endo-endo), toluene and JP-10.

A microvapor pressure apparatus and the technique employed for previous vapor pressure determinations (subsection 1) were used for these measurements. Data are presented in Table 38.

TABLE 35. SPECIFIC GRAVITY OF FUEL BLENDS

Sample	60°/60°F
7263-43, JP-10	0.9391
7263-44	1.0489
7263-45	1.0176
7263-46	0.9889
7263-47	0.9615
7263-48, RJ-5G	1.0836

TABLE 36. GAS CHROMATOGRAPHIC ANALYSIS OF THREE JP-9 FUELS

Component and Retention Time (min.)	Weight Percent*		
	Code 7262-50	Code 7277-51	Code 7277-52
2.65	0.24	-	-
2.78	9.93	8.31	5.94
2.97	0.50	0.44	-
Total MCH	10.67	8.71	5.94
7.05	66.68	66.90	70.49
7.50	2.37	2.35	2.52
Total JP-10	69.05	69.25	73.01
14.08	0.52	0.40	0.40
14.19	0.43	0.43	0.45
14.56	0.65	0.46	0.70
15.31	18.67	20.46	19.49
17.10	-	0.24	-
Total RJ-5	20.27	21.99	21.04

*Appropriate response factors applied.

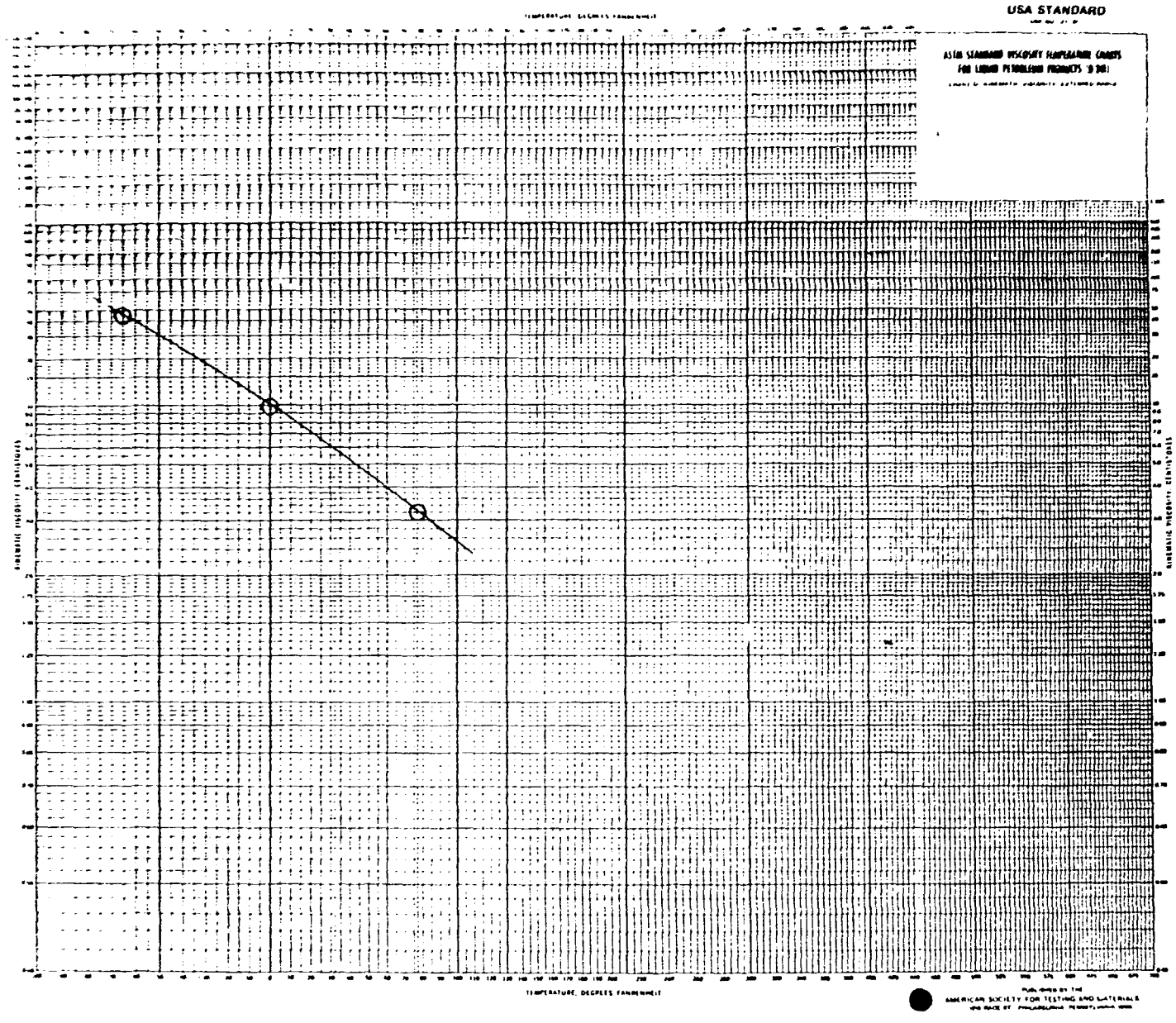

Figure 21. Fuel 7264-50, kinematic viscosity, extended range, for JP-9 fuel.

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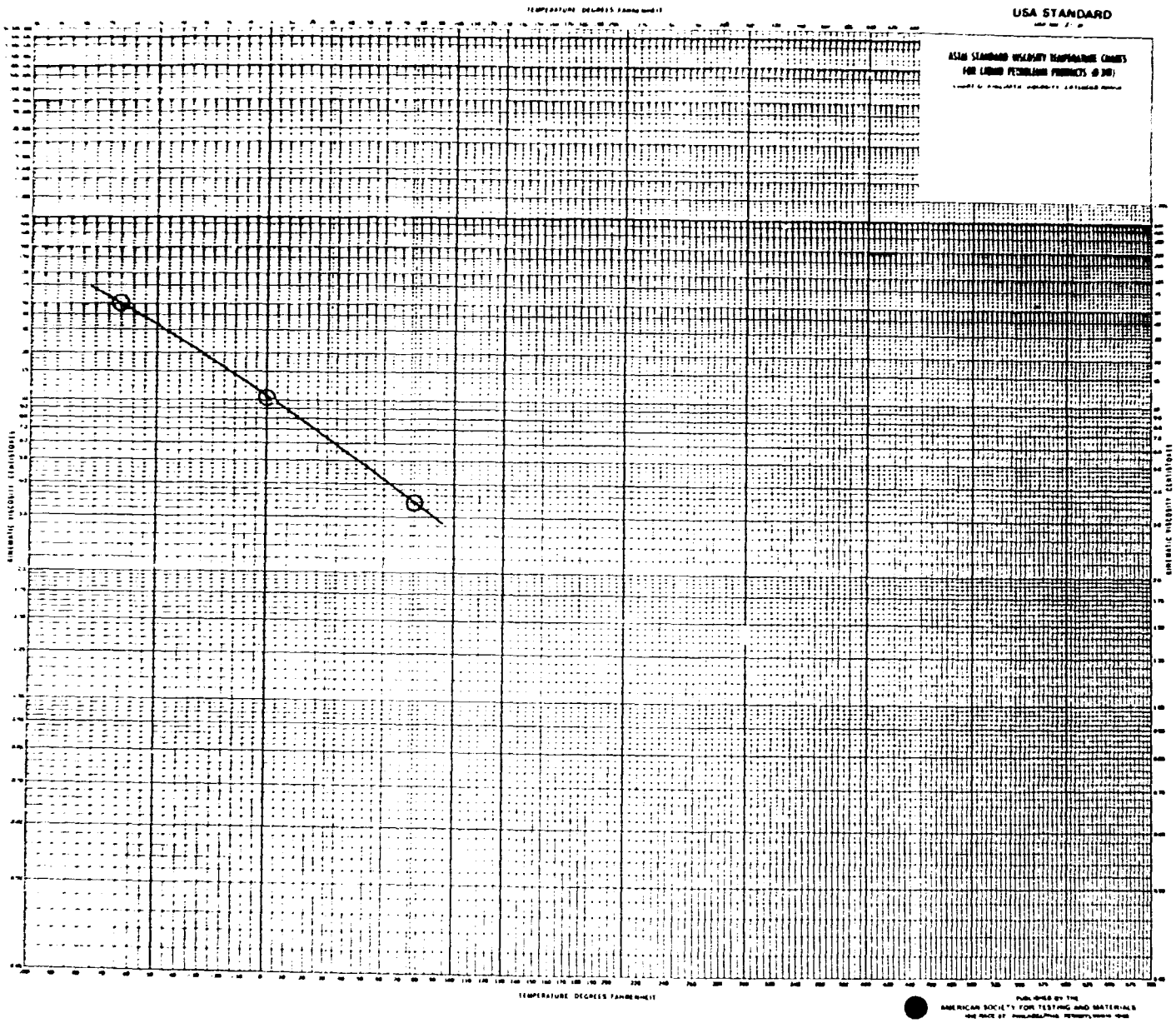

Figure 22. Fuel 7277-51, kinematic viscosity, extended range, for JP-9 fuel.

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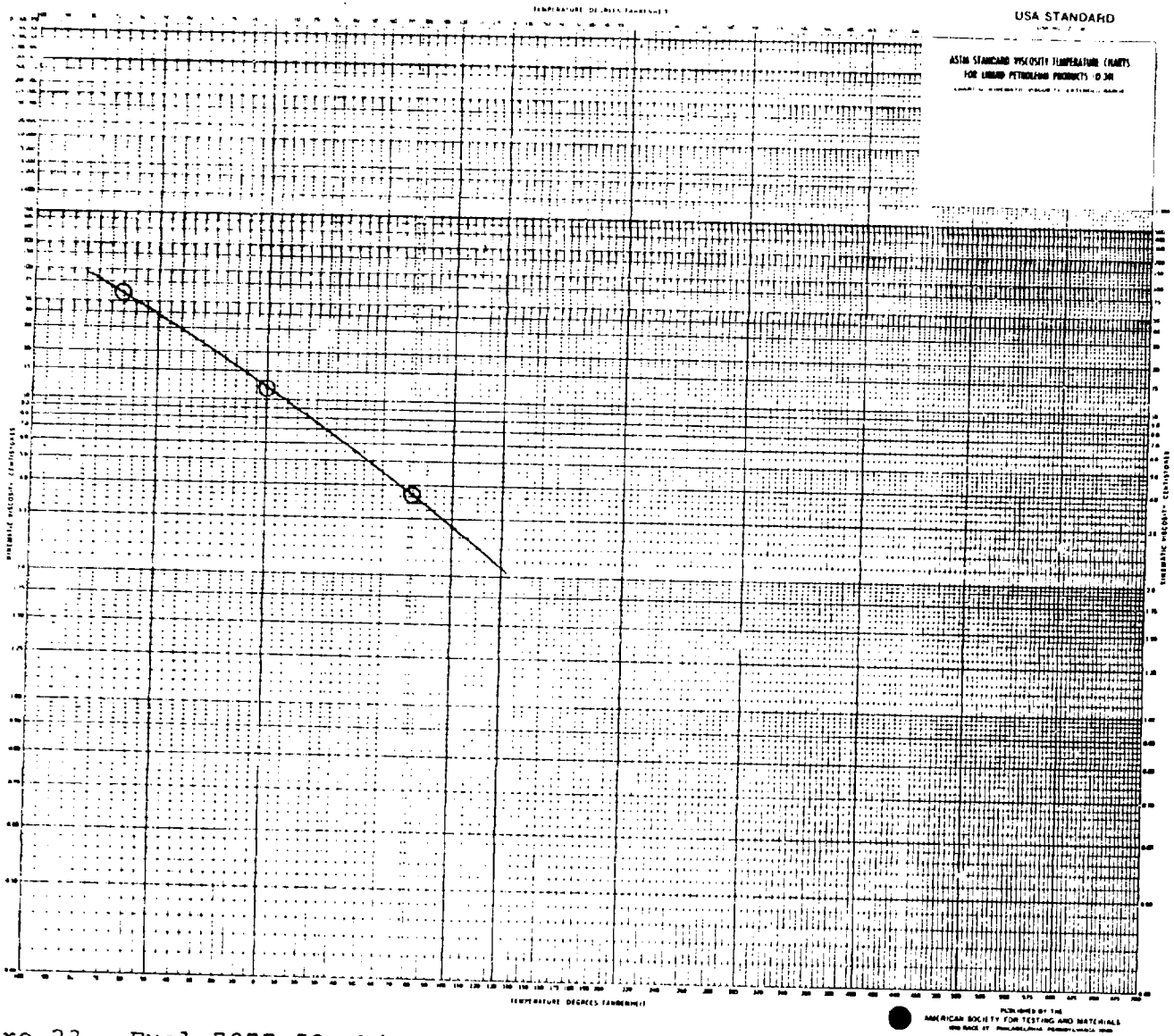

Figure 23. Fuel 7277-52, kinematic viscosity, extended range, for JP-9 fuel.

TABLE 37. PROPERTIES OF JP-9 FUEL SPECIMENS

		7264-50	7277-51	7277-52	4-55-930
Vapor Pressure (torr)	32°F	6	5	5	5
	77°F	16	14	14	13
	104°F	27	25	25	23
	136°F	51	45	45	-
	140°F	-	-	-	45
Kinematic Viscosity (Centistokes)	-65°F	45.95	50.49	59.76	53.40
	0°F	9.87	10.35	11.73	10.90
	77°F	3.22	3.39	3.65	3.49
Specific Gravity	60°F	0.9474	0.9532	0.9603	-

TABLE 38. VAPOR PRESSURE OF HIGH DENSITY FUEL BLENDS

Blend Composition by Weight	Pressure, torr 32°F	77°F	104°F	140°F
RJ-5G (endo-endo)	1.9	4	6	10
80% RJ-5G, 20% JP-10	4.3	7.5	10	14.5
60% RJ-5G, 40% JP-10	6.3	10.5	13.5	18.5
40% RJ-5G, 60% JP-10	7.5	12	15	19.5
JP-10 (exo-THD)	9	14	18	23.5
99% RJ-5G, 1% toluene	2.9	7	11	18
98% RJ-5G, 2% toluene	3.6	8	12	20.5

10. LOW TEMPERATURE PROPERTIES AND GC ANALYSIS OF HIGH DENSITY FUEL TEST BLENDS

Three high density fuel blends were prepared and evaluated for their tendency to freeze at -65°F. Specimens were also subjected to detailed gas chromatographic analysis and the determination of kinematic viscosity at -65°F.

Blends were prepared by mixing measured volumes of the individual components. Nominal compositions were as follows:

Blend A	Ashland RJ-5	52%
	RJ-4	27%
	JP-10 (exo-THD)	21%
Blend B	RJ-5G (endo-endo)	60%
	JP-10 (exo-THD)	40%
Blend C	Ashland RJ-5	60%
	JP-10 (exo-THD)	16%
	RJ-4	24%

The RJ-5G and JP-10, coded 7263-43 and 7263-48 respectively, were used in formulating the blends. Data for the analysis of these components are presented in subsection 7 of this section.

In order to determine if any of the blends could be frozen at temperatures down to -65°F, borosilicate glass vials containing the specimens were placed in a low temperature bath (Blue M Electric Company, Model LTB-1-75C) maintained at -65°F. Samples were periodically agitated and occasionally cycled in temperature during a 24-hour period. During this time, samples showed no indication of freezing. After 24 hours, an attempt was made to nucleate crystallization by the addition of seed crystals. No pure endo-end0 isomer was available for this purpose, but the solid exo-t-exo pentacyclic dimer was on hand and, therefore, was added.

Samples were maintained in the bath for an additional 48 hours without the development of further crystals, although the seed crystals did not dissolve. During this residence time, samples were again periodically agitated and temperature cycled.

The kinematic viscosity of each blend was measured at -65°F, and the following values were obtained:

Blend A	601.2 centistokes
Blend B	413.2 centistokes
Blend C	961.7 centistokes

Blends were analyzed by gas chromatography using a Perkin-Elmer Model 3920 chromatograph and conditions described in A of Appendix B. Analyses are presented in Table 39. The volume percent of each component was calculated and these values were summed to obtain the volume percent of each fuel constituent. Several low-boiling components were observed for Blend B, and previous analysis in subsection 7 has shown them to be minor components of RJ-5G. Chromatographs are presented in Figures 24-26.

11. PHYSICAL PROPERTIES OF RJ-6 FUEL BLEND

A blend of RJ-6 fuel, comprised of 60 volume percent Ashland type RJ-5 and 40 volume percent JP-10, was prepared. This fuel was the subject of vapor pressure, heat of combustion, specific gravity and viscosity tests. Additionally, the fuel was analyzed by gas chromatography to determine purity and verify composition.

A measurement of vapor pressure at 300°F was conducted using the vapor reflux method (6). Figure 27 illustrates a plot of a series of temperature/pressure equilibration points obtained

TABLE 39. GAS CHROMATOGRAPHIC ANALYSIS OF TEST FUEL BLENDS

Retention Time (minutes)		Volume Percent*		
		Blend A	Blend B	Blend C
		-	0.39	-
6.19		-	0.23	-
6.46		-	0.19	-
8.74		20.40	39.39	15.51
9.29		0.62	0.47	0.48
	Total exo-THD	21.02	39.86	15.99
10.57		2.30	-	1.71
10.67		1.15	-	0.53
11.14		0.91	-	0.77
11.26		0.64	-	0.55
11.39		2.23	-	1.88
11.58		5.66	-	5.07
11.72		5.35	-	4.74
11.86		0.70	-	0.63
12.34		0.19	-	-
12.64		8.17	-	7.37
	Total RJ-4	27.30	-0-	23.25
16.36		3.93	1.14	4.49
16.66		8.66	1.66	9.98
17.15		0.62	-	0.76
17.54		38.47	56.53	45.52
	Total RJ-5	51.68	60.14	60.75

* Response factors calculated and applied

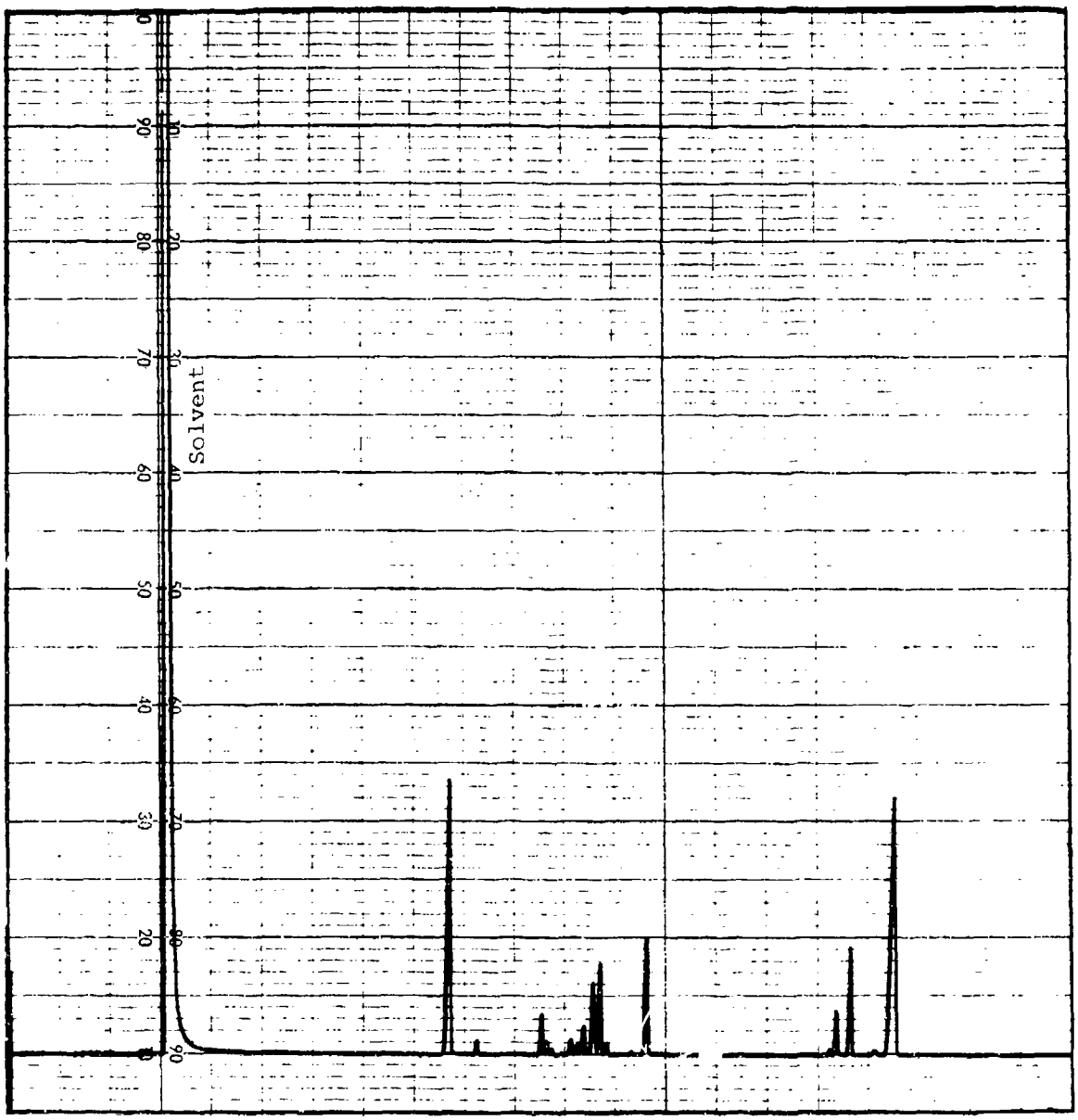

Figure 24. Gas chromatogram of Test Blend A.

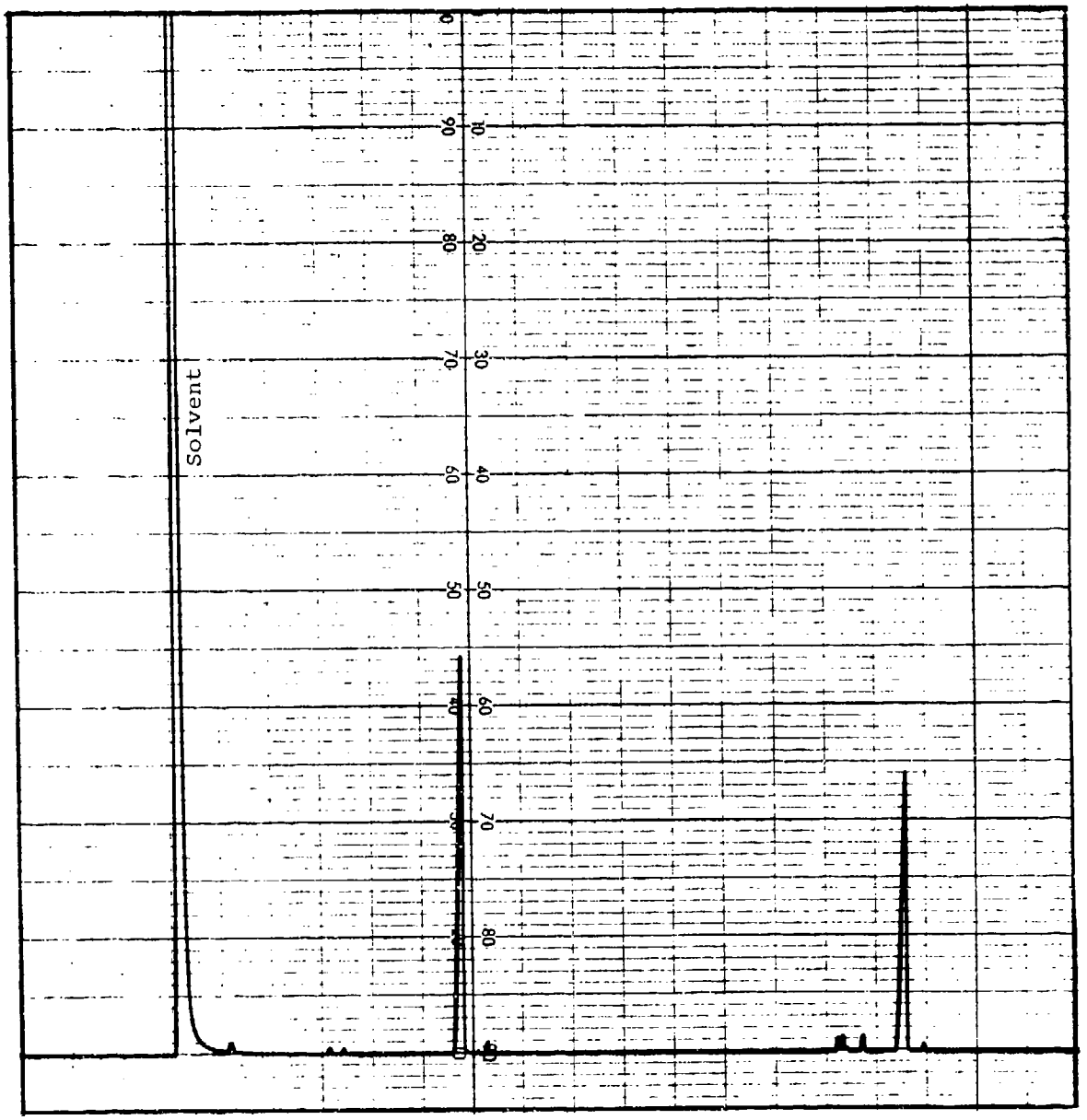

Figure 25. Gas chromatogram of Test Blend B.

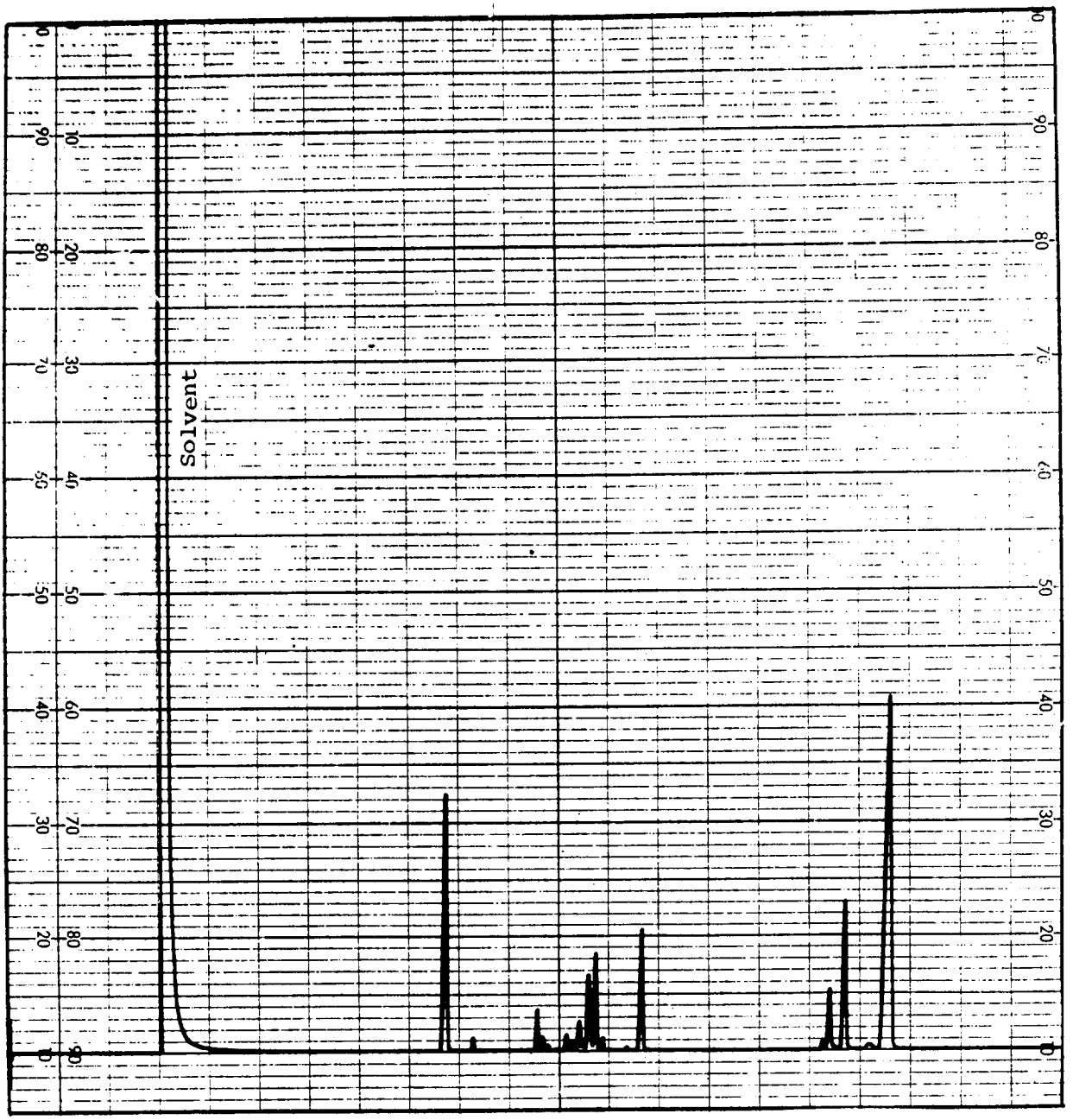

Figure 26. Gas chromatogram of Test Blend C.

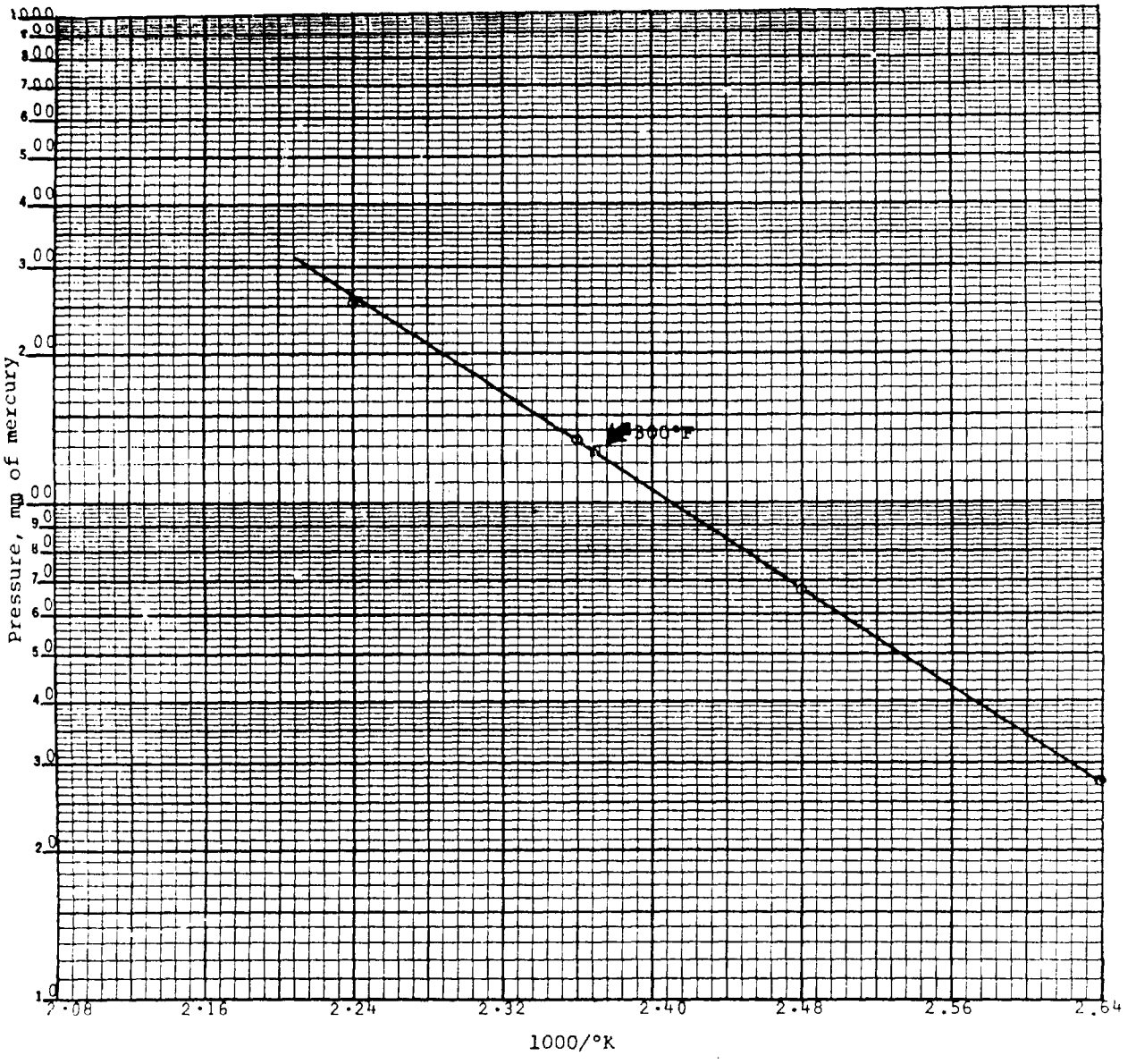

Figure 27. Plot of log vapor pressure versus reciprocal absolute temperature for test fuel blend.

by this technique. The vapor pressure at 300°F is presented in Table 40.

TABLE 40. PHYSICAL PROPERTIES OF RJ-6 BLEND CONTAINING 60% ASHLAND RJ-5, 40% JP-10 BY VOLUME

Physical Property	
Vapor Pressure, 300°F	128 torr
Kinematic Viscosity, -40°F	159.3 centistokes
-65°F	508.2 centistokes
Specific Gravity, 60°F	1.0269
Heat of Combustion, Gross	18,958 BTU/lb
	18,931 BTU/lb
	Av. 18,945 BTU/lb
Heat of Combustion, Net	17,941 BTU/lb

Kinematic viscosity was measured at -40°F and -65°F according to ASTM procedure D445. Specific gravity at 60°F was measured by the dilatometer technique. This information is also presented in Table 40.

Heat of combustion of the test blend was determined using the oxygen bomb calorimeter as described in ASTM D-240.

The blend was analyzed by gas chromatography using a Perkin-Elmer Model 3920 and conditions described in Appendix B. Results are presented in Table 41. The chromatogram is shown in Figure 28.

TABLE 41. GAS CHROMATOGRAPHIC ANALYSIS OF TEST RJ-6 BLEND

Retention Time, min		Volume Percent
8.71		39.93
9.22		0.40
	Total JP-10	40.33
16.30		4.61
16.59		10.54
17.04		.41
17.45		44.11
	Total RJ-5	59.67

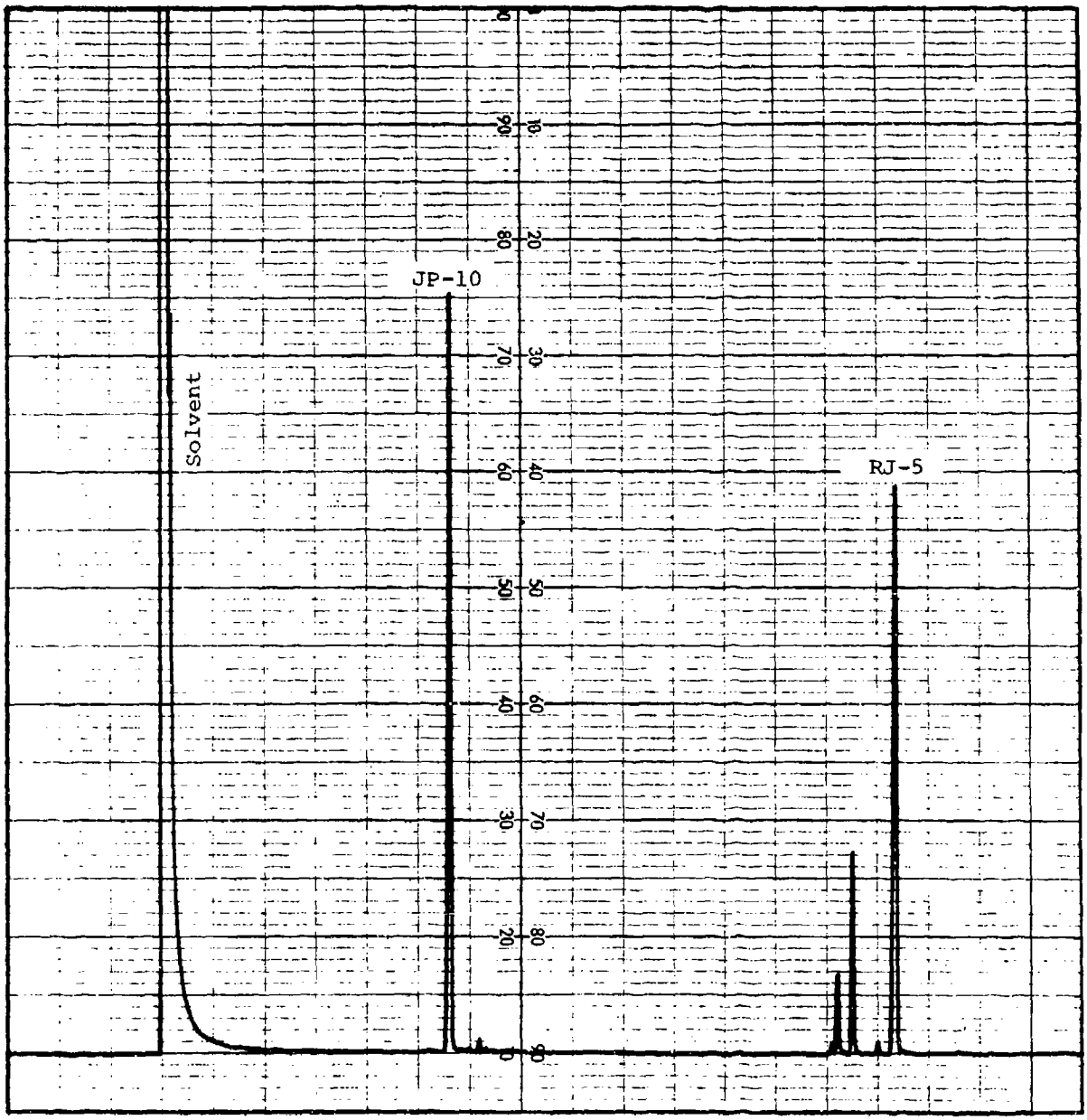

Figure 28. Gas chromatogram of test fuel blend.

12. IDENTIFICATION OF RJ-4 FUEL CONTAMINANTS

An obviously discolored specimen of RJ-4, taken from a flight test vehicle, was examined to determine the presence of contaminants. Additionally, a filter element used for filtration of the fuel was examined to determine the identity of metallic particles which may have resulted from fuel system component wear.

Procedure

The fuel was passed through a short column of 100-200 mesh silica gel and was completely colorless upon emerging from the column. The brown material retained by the gel was carefully rinsed with pentane to remove residual fuel and was then recovered from the gel by elution with chloroform and then methanol. Upon evaporation of the solvents, a dark brown, highly viscous material, which was insoluble in pentane or other hydrocarbon solvents, was obtained.

An infrared absorption spectrum of the brown material was recorded is shown in Figure 29. A gas chromatographic analysis was conducted on a chloroform solution of the material using a 50-meter glass capillary column coated with SF-96 stationary phase. The chromatogram, shown in Figure 31 and tabulated in Table 42, shows over twenty components with the most abundant being present at about the 14% level.

The fuel filter element was analyzed by energy-dispersive x-ray spectrometry. The minute metallic particles were determined to be aluminum, this being the only detectable major element.

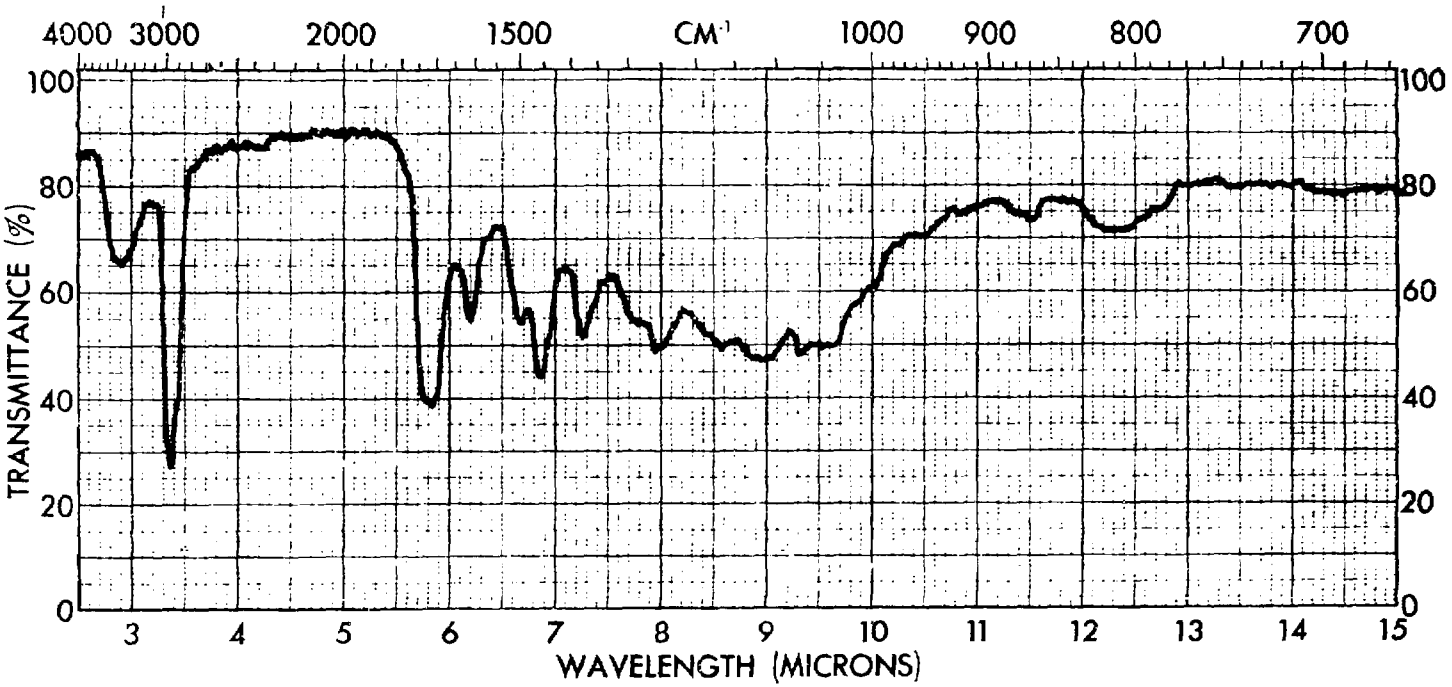

Figure 29. Infrared absorption spectrum of brown residue isolated from fuel.

Conclusions

The infrared absorption spectrum obtained for the isolated contaminants contains a band at ∿5.8 μm which is characteristic of a carbonyl grouping and a band at ∿3.0 μm showing hydroxy character. The spectrum has similarities to those of a number of plasticizers and one could not conclusively rule out the presence of a small amount of such a material. However, the spectrum shown in Figure 30 very closely resembles that of degraded RJ-4 as described in a recent report (7) by Bendix Corporation. Degradation of RJ-4 results in the formation of peroxidic carbonyl by oxidative degradation. These characteristics are shown in the residue spectrum of Figure 30. A general infrared absorption increase between 7 and 13 μm is reported for degraded RJ-4, and this also is shown in the spectrum of Figure 30. In summary, the spectrum obtained for the isolated fuel contaminant matches in detail the IR data reported for degraded RJ-4.

Since degradation can take place in varying degrees and by both hydrolysis and oxidative reactions, one would expect the degradation products to be a mixture of compounds, a fact demonstrated by the chromatogram and data of Figure 30 and Table 42. The referenced report describes the material as "a sticky, brown, resinous material," a description which fits the isolated contaminant.

The data strongly support the conclusion that the contaminant is not due to plasticizers extracted from the fuel bladder, but results from hydrolytic/oxidative degradation of the fuel.

A more specific identification of the individual components of the brown residue could have been obtained by combined GC/mass spectrometric analysis if the need warranted this approach.

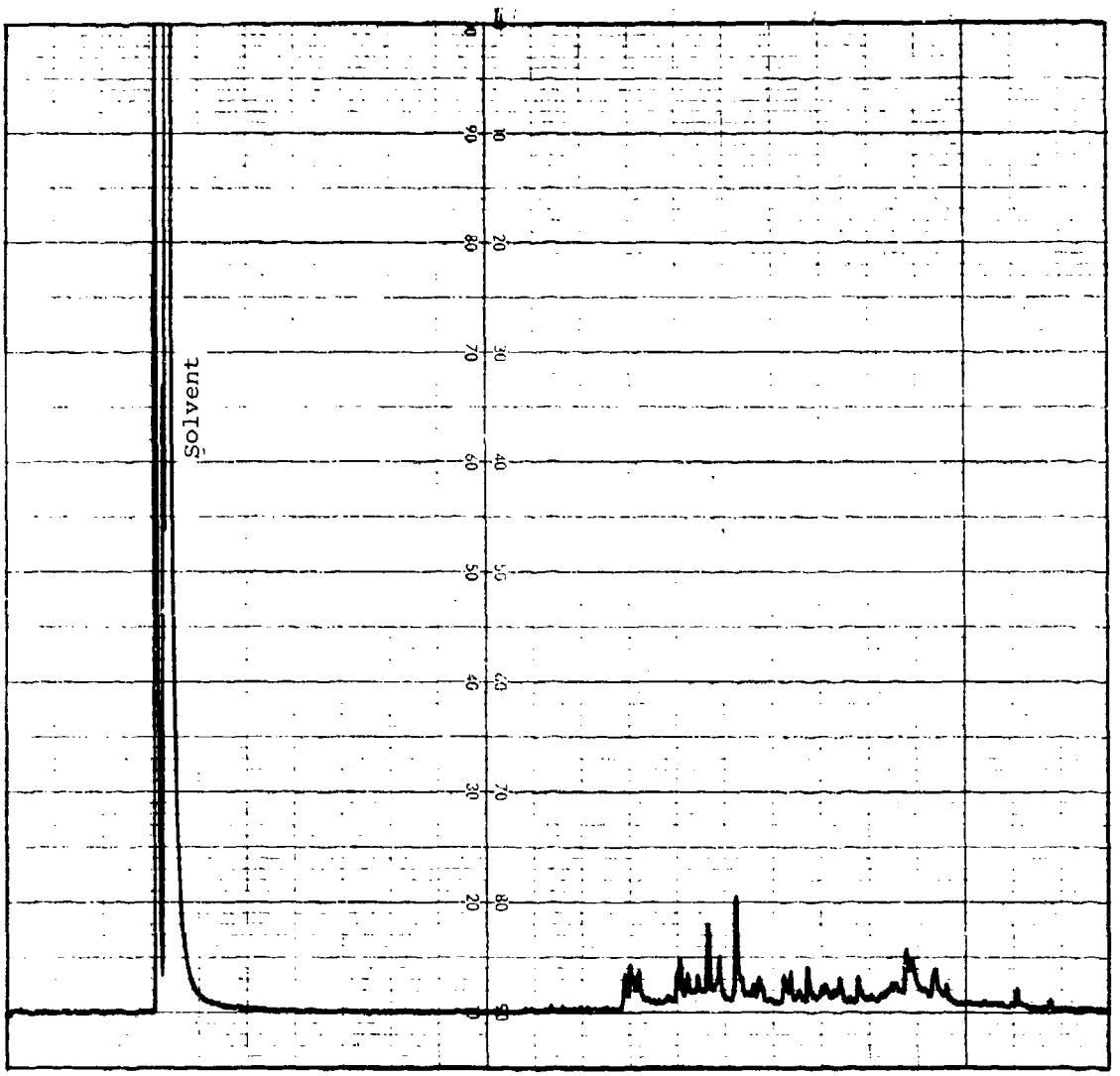

Figure 30. Gas chromatogram of brown fuel residue.

TABLE 42. GAS CHROMATOGRAPHIC DATA FOR FUEL RESIDUE

ACTUAL RUN TIME: 24.017 MINUTES

RT	AREA		AREA %
12.81	88	BV	2.719
12.92	143	VV	4.405
13.09	133	VB	4.105
13.71	28	BB	.854
13.90	40	BV	1.222
13.97	90	VV	2.763
14.12	195	VV	6.003
14.55	192	VV	5.914
14.78	178	VV	5.491
15.15	361	VV	11.118
15.62	151	VB	4.642
16.16	143	BV	4.386
16.48	52	VV	1.590
16.68	113	VV	3.491
17.04	119	VV	3.648
17.33	120	VV	3.693
17.72	127	VV	3.921
18.42	210	VV	6.451
18.72	474	VV	14.599
19.30	187	VV	5.759
19.55	66	VB	2.040
20.35	11	BB	.331
21.69	28	BB	.853

TOTAL AREA = 3250

PROCESSED DATA FILE: *FRC04

TOTAL AREA % = 100.000

RAW DATA FILE: *RAW04

13. PROPERTIES AND ANALYSIS OF JP-9 AND RJ-5 BLENDS

Two high density fuel specimens, designated JP-9 Blend 24 and RJ-5 Blend (McCoy), were analyzed by gas chromatography to determine properties and composition. The heat of combustion and specific gravity of each fuel were also determined. Kinematic viscosity was determined as a function of temperature for the RJ-5 blend.

Chromatographic analyses were conducted on a Perkin-Elmer 3920-B gas chromatograph equipped with a 50-meter glass capillary column coated with SF-96 stationary phase. Detection was by FID. Relative response factors were determined for RJ-5 and JP-10 for use in calculating the JP-9 composition. Chromatographic data are presented in Tables 43 and 44.

Heat of combustion was determined by ASTM procedure D240-64. Values are presented in Table 45.

Specific gravity was determined at 60°F using a dilatometer, and kinematic viscosity was determined as a function of temperature using ASTM procedure D445. These data are presented in Table 46. The viscosity/temperature relationship is illustrated in Figure 31.

14. PROPERTIES AND ANALYSIS OF JP-10 FUEL

Several physical properties were measured on a specimen of JP-10 fuel in support of toxicology studies being performed by the Air Force Aerospace Medical Research Laboratory (AMRL). All properties were measured at 70°F. Density was determined by the dilatometer method and kinematic viscosity was measured using ASTM procedure D445. Vapor pressure was determined by the micromethod using an apparatus described in subsection 1 and employed

TABLE 43. GAS CHROMATOGRAPHIC ANALYSIS OF JP-9 BLEND 24

Retention Time (minutes)	Weight Percent*	
4.61	0.95	
4.91	8.46	
5.13	0.76	
5.65	0.60	
MCH & other components		10.77%
13.78	65.36	
14.14	0.48	
14.41	1.22	
Total JP-10		67.06%
21.95	0.29	
22.45	0.63	
23.22	21.25	
Total RJ-5		22.17%

TABLE 44. GAS CHROMATOGRAPHIC ANALYSIS OF RJ-5 FUEL (MCCOY)

Retention Time† (minutes)	Weight Percent
4.51	0.337
17.81	1.806
17.94	5.885
18.28	19.694
18.34	1.475
18.73	0.710
19.19	69.356
19.50	0.737

* Appropriate response factors calculated.

† Chromatographic conditions were varied slightly from the previous run shown in Table 43.

TABLE 45. HEAT OF COMBUSTION OF TEST FUELS

	Gross BTU/lb		Net BTU/lb
JP-9, Blend 24	19,024		
	19,002		
	Avg.	19,013	17,941
RJ-5 Fuel (McCoy)	18,794		
	18,837		
	Avg.	18,816	17,912

TABLE 46. ADDITIONAL PHYSICAL PROPERTIES OF TEST FUELS

	Specific Gravity	Kinematic Viscosity (Centistokes)		
	60°F	-65°F	0°F	77°F
JP-9 Blend 24	0.9465	-	-	-
RJ-5 Fuel (McCoy)	1.0802	12,030	190.8	19.08

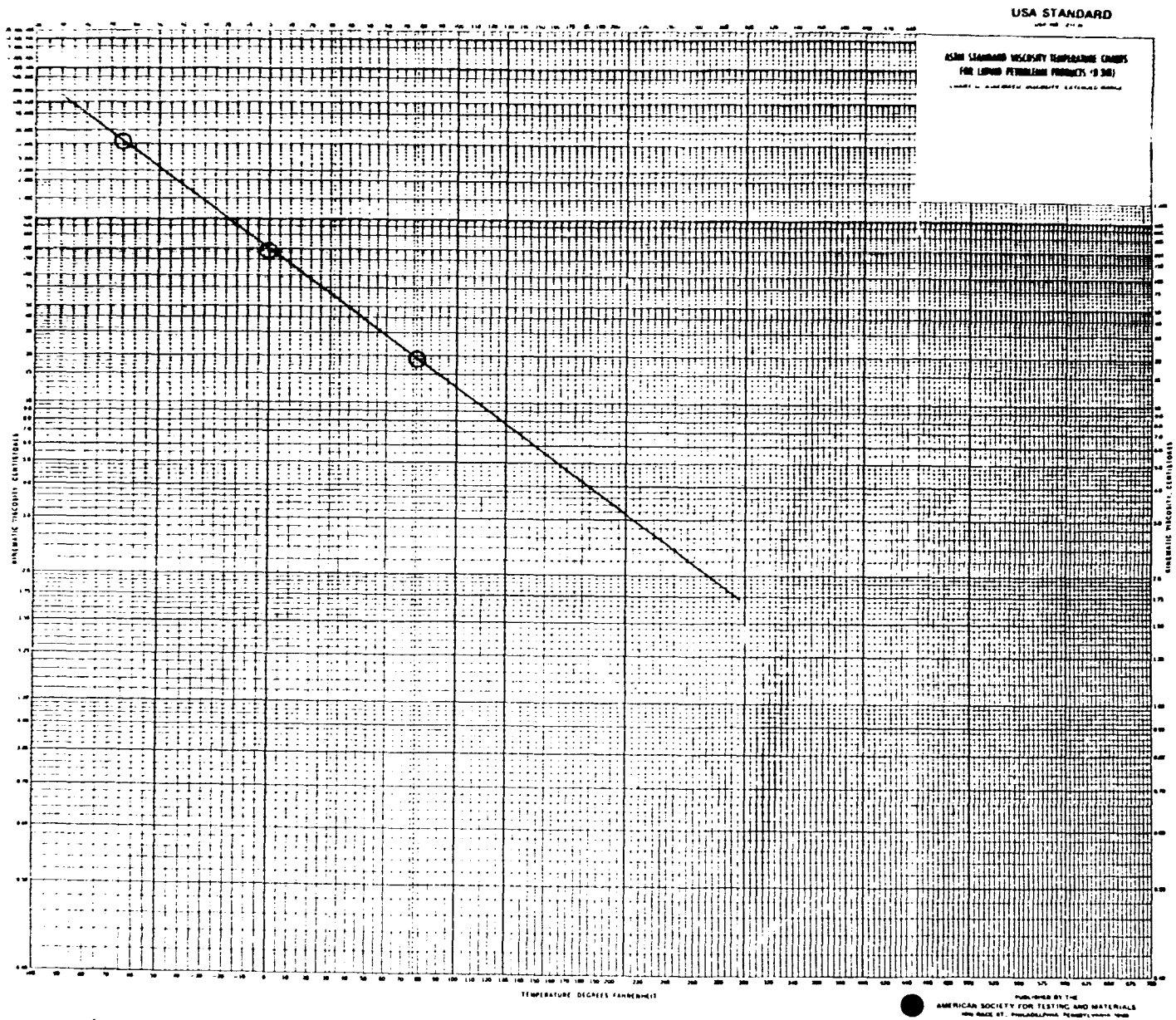

Figure 31. Viscosity/temperature plot for RJ-5 blend (McCoy).

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in ASTM D2551-71. This is a static test method of the kind required for approaching a true vapor pressure measurement, i.e., a measurement which does not of itself change the fuel composition.

Data are presented in Table 47.

TABLE 47. PROPERTIES OF JP-10 FUEL AT 70°F

Kinematic Viscosity (centistokes)	3.267
Density (grams per cc)	0.9354
Vapor Pressure (torr)	12

A chromatographic analysis of the specimen was conducted using a Perkin-Elmer 3920-B gas chromatograph having a 50-meter glass capillary column coated with SF-96 liquid phase. The chromatogram is shown in Figure 32 and data are presented in Table 48.

TABLE 48. GAS CHROMATOGRAPHIC DATA FOR JP-10 FUEL

SAMPLE: JP-10

ZERO METHOD: TEST4

ACTUAL RUN TIME: 22.833 MINUTES

RT	AREA	AREA %
8.92	10599 BB	97.631
9.19	83 BB	.765
9.39	174 BB	1.605

TOTAL AREA = 10857 TOTAL AREA % = 100.000

PROCESSED DATA FILE: *PRC04 RAW DATA FILE: *RAW04

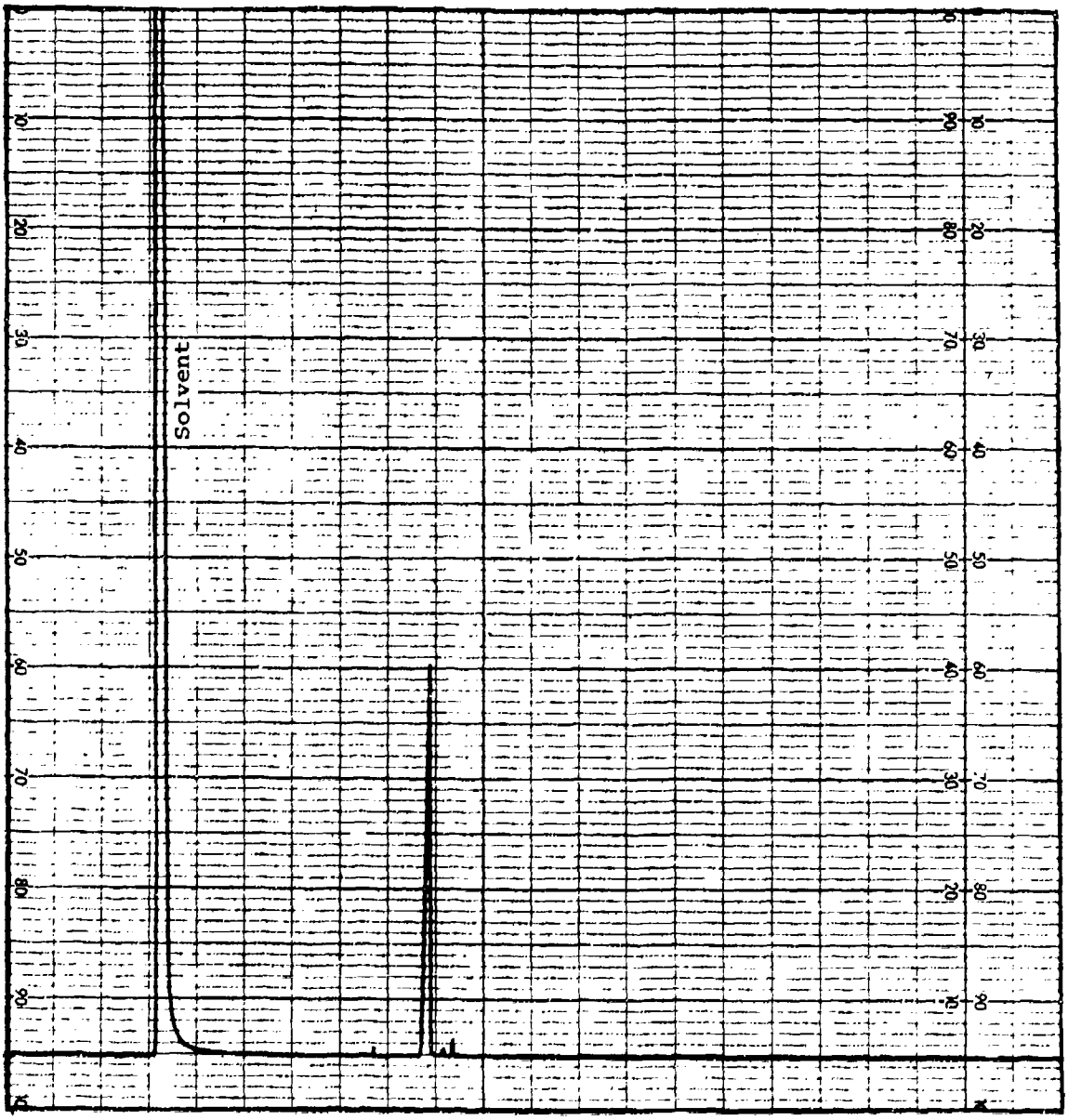


Figure 32. Gas chromatogram for JP-10 fuel.

SECTION III

SPECIAL INVESTIGATIONS

A number of special investigations were conducted to provide data for on-going fuels programs, to aid in solving operation problems and to provide data to satisfy health and safety needs.

1. ANALYSIS OF FUEL STORAGE TANK EMISSIONS

Concentrations of hydrocarbons, present in the air displaced from large underground fuel storage tanks during a fill operation, were investigated. These tests, which took place at a fuel storage facility in Area C of WPAFB, were conducted to provide the Air Force with data to aid in evaluting the compliance of such emissions with current air quality regulations. The measurements were conducted while two vapor-containing 50,000 gal tanks were filled with JP-4. The fuel was shown by subsequent tests of its vapor pressure and distillation characteristics to be a typical JP-4.

Experimental

The basic analytical instrument employed was an AID Model 511 Portable Gas Chromatograph (Analytical Instrument Development, Inc.) having a flame ionization detection system. The unit contained lecture-size bottles of hydrogen and air which were used to produce the small flame required for operation of the detector. A similar bottle of nitrogen was contained in the instrument for use as a carrier gas. The supply of these gases was sufficient for about 8 hours of operation. A total-hydrocarbon analyses were required, the chromatograph was used without an analytical column.

Though the instrument cannot be operated in an atmosphere in which hydrocarbons reach a combustible concentration, the apparatus, in the employed configuration, had been used to sample methane at concentrations up to the pure gas without creating a hazardous situation. Analysis of the sample vapors, which took place at regular intervals during the tank filling operation, involved merely closing the valve to the pump and rotating the gas sampling valve.

One limitation of the flame ionization detector is its non-linear response to high concentrations of hydrocarbons. Bench top experiments showed that JP-4 vapors can be in the non-linear response range of this detector. Thus, the analytical procedure involved a 15-fold dilution of the sample stream with pure nitrogen prior to analysis. After passing through the analytical unit, the sample stream was expelled to an outside area. The primary purpose of the fixed dilution step was to reduce the hydrocarbons to a level where the detector response was directly proportional to hydrocarbon concentrations. This step also served the safety purpose of lowering the hydrocarbon concentration of the sample stream.

Vapors were withdrawn from the tank vent which was located an estimated 15 feet above ground level, through 100 feet of aluminum tubing having an O.D. of 0.125 inch and an I.D. of 0.0625 inch. A flame arrester, consisting of a 0.25 inch Crawford fitting cap having four 0.020 diameter holes for entrance of sample, was placed at the end of the sample intake tube. The arrangement of various components of the apparatus is shown in Figure 33. Care was taken to insure that all components of the system were electrically grounded.

The chromatographic unit, though capable of operating by self-contained batteries, was powered from a 115 volt A.C. source. A

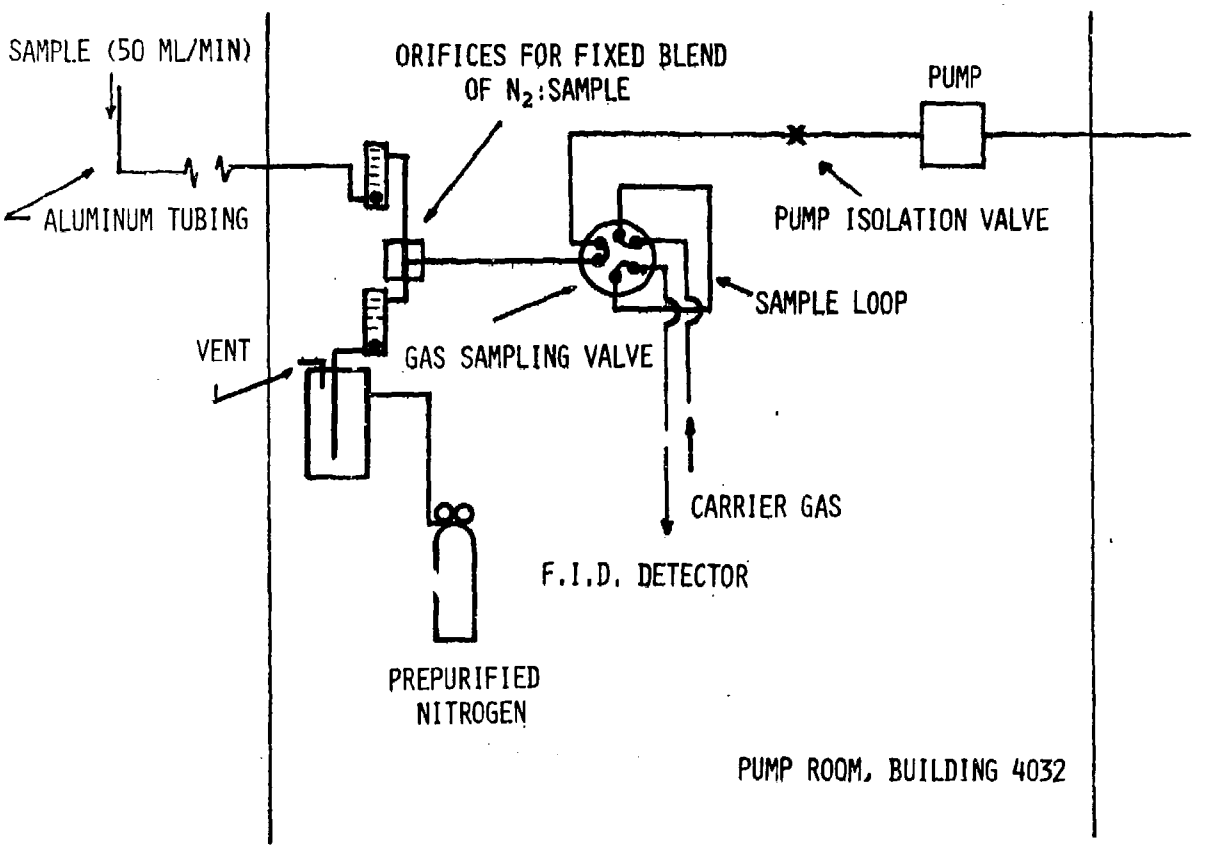


Figure 33. Schematic arrangement of apparatus.

Doerr 1/4 hp, 115 volt pump was used to withdraw sample from the tank vent and blend it with nitrogen from a small cylinder.

A special nitrogen/sample-vapor blending device was constructed to provide the required dilution. The quantity of gas, Q, which passes through a tube, across a pressure differential of P_2-P_1, is governed by the Poiseuille equation (8):

$$Q = \frac{0.16\ d^4}{\eta\ \ell} (P_2^2 - P_1^2) \text{ liters torr/sec} \qquad (3)$$

where η = the viscosity of the gas
d = the tube diameter
ℓ = length of tube at a temperature of 300°K

The blending device consisted of sections of tubing of the length and diameter required to allow a 15-fold greater amount of nitrogen than sample to be drawn through the system by the pump. All terms in equation 1 remain constant possibly except P_2 and P_1 (atmospheric pressure and pump pressure). Changes in pressure, however, act equally on both gas streams and do not affect the blending ratio.

The nitrogen was drawn from a chamber into which a slight surplus of that gas flowed but which was vented to the atmosphere. Rotameters were used to monitor both sample and diluent flows. Actual gas flows were 50 ml/min for the sample stream and 750 ml/min for the nitrogen stream.

Standard mixtures of methane in air were used for calibrating the system. These standards were drawn through the 100-foot sampling line in the same manner as the fuel vapors.

The plot of detector response vs concentration, which was recorded just prior to actual vapor analyses, is linear for mixtures up to 100% methane (Figure 34).

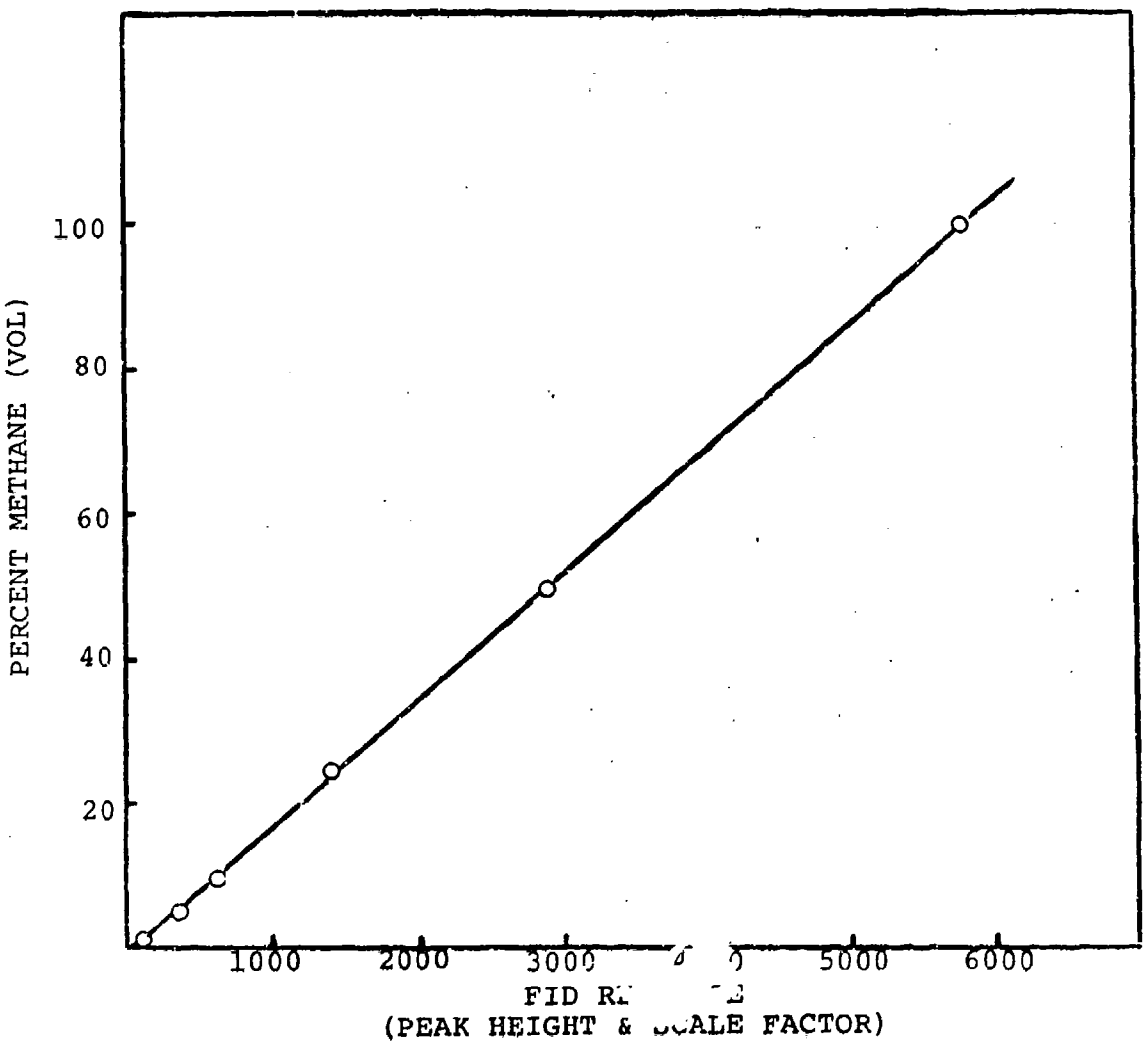


Figure 34. Calibration of analytical system using air/methane mixtures.

Description of Tests

Hydrocarbon emissions from two tanks were measured. Tank #283 had been cleaned one week before measurements were performed. Immediately after cleaning, 12,500 gallons of JP-4 were added to the tank. On the day before taking measurements, 5,200 gallons of fuel were removed leaving 7,300 gallons. Tank #285 was cleaned in the morning prior to conducting measurements. In the afternoon of that same day 5,200 gallons of JP-4 were added to the tank.

Tests were conducted by housing the analytical apparatus described in the previous section in the pump room of Building 4032. Sample intake and exhaust lines were passed through an exhaust fan opening in the wall about 7 feet above the floor. The door to the room remained closed during tests and the room atmosphere was continuously monitored for the accumulation of hazardous vapors using a portable vapor detector. Tests commenced only after inspection of apparatus, test plan and emergency shutdown procedures by appropriate base safety personnel.

During tests, the two tanks were filled by means of underground pipelines from the tank-farm. Calibration gases were passed through the test apparatus immediately prior to the tests and again before changing the sample line to the vent of the second tank. The sample line was placed under the cover of the vent next to the flame arrester. The vent was in no way changed or disassembled during sampling.

Results and Discussion

Tanks were filled at an average rate of 460 gal/min as shown in Figure 35 where the number of gallons delivered are plotted against fill-time. Tables 49 and 50 present total hydrocarbon values in volume percent as methane equivalents. Data given in Tables 49 and 50 are plotted in Figures 36 and 37. Values for the volume

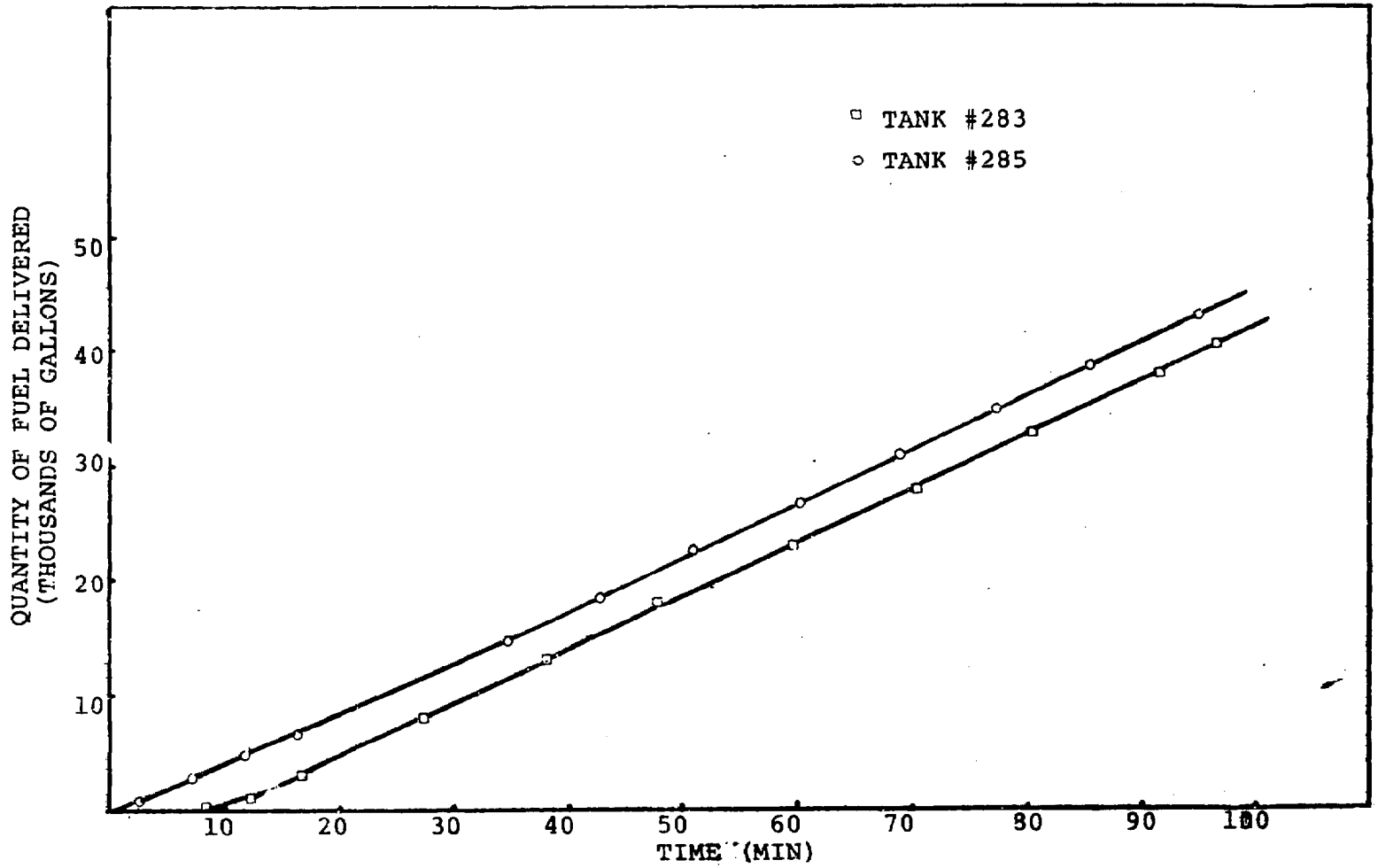


Figure 35. Amount of fuel delivered as a function of time.

TABLE 49. CONCENTRATION OF HYDROCARBON EMISSIONS FROM FUEL TANK #283

Elapsed time (minutes)	Fuel[a] delivered (thousands of gallons)	Total[b] hydrocarbons (%)	Elapsed time (minutes)	Fuel[a] delivered (thousands of gallons)	Total[b] hydrocarbons (%)
0	(fuel requested)	N.D.[c]	41	14.5	50.0
			42	15.0	48.4
7.5	(flow started)	N.D.	43	15.4	50.0
			44	15.9	49.0
9	-	4.4	45	16.3	51.8
10	0.2	5.4	46	16.8	51.6
11	0.7	17.5	47	17.3	49.5
12	1.2	43.1	48	17.7	49.0
13	1.6	46.6	49	18.2	48.3
14	2.1	46.6	50	18.6	50.6
15	2.5	44.8	51	19.1	49.5
16	3.0	46.0	52	19.6	47.2
17	3.5	46.6	53	20.0	48.4
18	3.9	48.3	54	20.4	50.1
19	4.4	47.7	55	20.9	50.1
20	4.8	47.5	56	21.4	47.8
21	5.3	47.2	57	21.9	47.1
22	5.8	46.0	58	22.3	48.6
23	6.2	48.3	59	22.8	47.5
24	6.7	47.2	60	23.2	49.5
25	7.1	48.3	62	24.2	50.5
26	7.6	45.4	65	25.5	51.0
27	8.1	48.9	67	26.5	50.0
28	8.5	48.3	70	27.8	51.0
29	9.0	46.6	72	28.8	53.0
30	9.4	41.9	75	30.1	54.0
31	9.9	47.7	77	31.1	53.5
32	10.4	48.9	80	32.4	54.0
33	10.8	48.5	82	33.4	54.5
34	11.3	47.8	86	35.2	55.0
35	11.7	48.9	88	36.1	54.0
36	12.2	49.5	91	37.5	53.0
37	12.7	48.9	94	38.9	57.0
38	13.1	49.5	96	40.2	50.0
39	13.6	50.7	98	40.2	5.0
40	14.0	48.4	100	40.2	N.D.

[a] Tank contained 7,300 gallons before flow started
[b] Given in volume % as methane equivalents.
[c] N.D. - none detected

TABLE 50. CONCENTRATION OF HYDROCARBON EMISSIONS FROM FUEL TANK #285

Elapsed time (minutes)	Fuel[a] delivered (thousands of gallons)	Total[b] hydrocarbons (%)	Elapsed time (minutes)	Fuel[a] delivered (thousands of gallons)	Total[b] hydrocarbons (%)
2	-	flow started	44	20.2	42.0
3	-	0.5	47	21.6	39.2
4	1.8	30.0	50	23.0	42.6
5	2.3	32.8	53	24.4	40.0
6	2.8	35.0	56	25.8	42.0
7	3.2	34.3	59	27.1	43.3
8	3.7	34.9	62	28.5	42.0
9	4.1	34.9	65	29.9	43.3
10	4.6	36.0	68	31.3	43.3
12	5.5	39.2	71	32.7	44.0
14	6.4	38.5	74	34.0	44.8
17	7.8	37.1	77	35.4	44.0
20	9.2	35.7	80	36.8	45.8
23	10.6	34.9	83	38.2	46.1
26	12.0	35.7	86	39.6	49.6
29	13.3	35.7	89	40.9	46.1
32	14.7	38.5	92	42.3	45.8
35	16.1	37.3	95	43.7	47.2
38	17.5	37.1	97	43.7	5.0
41	18.9	37.3	99	43.7	N.D.[c]

a Tank contained 7,300 gallons before flow started
b Given in volume % as methane equivalents
c N.D. - none detected

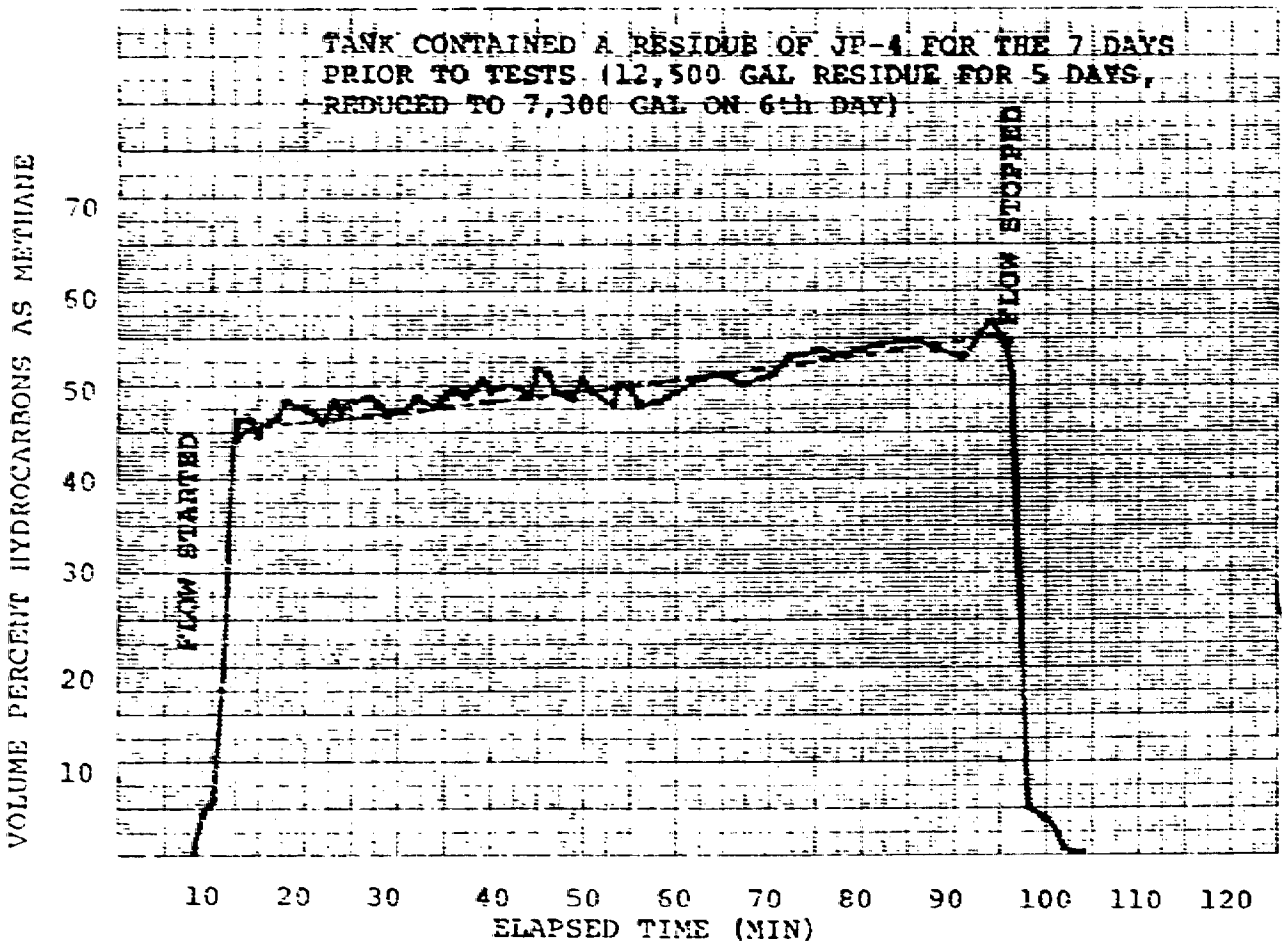


Figure 36. Hydrocarbon emissions from tank #283 during JP-4 fill operation.

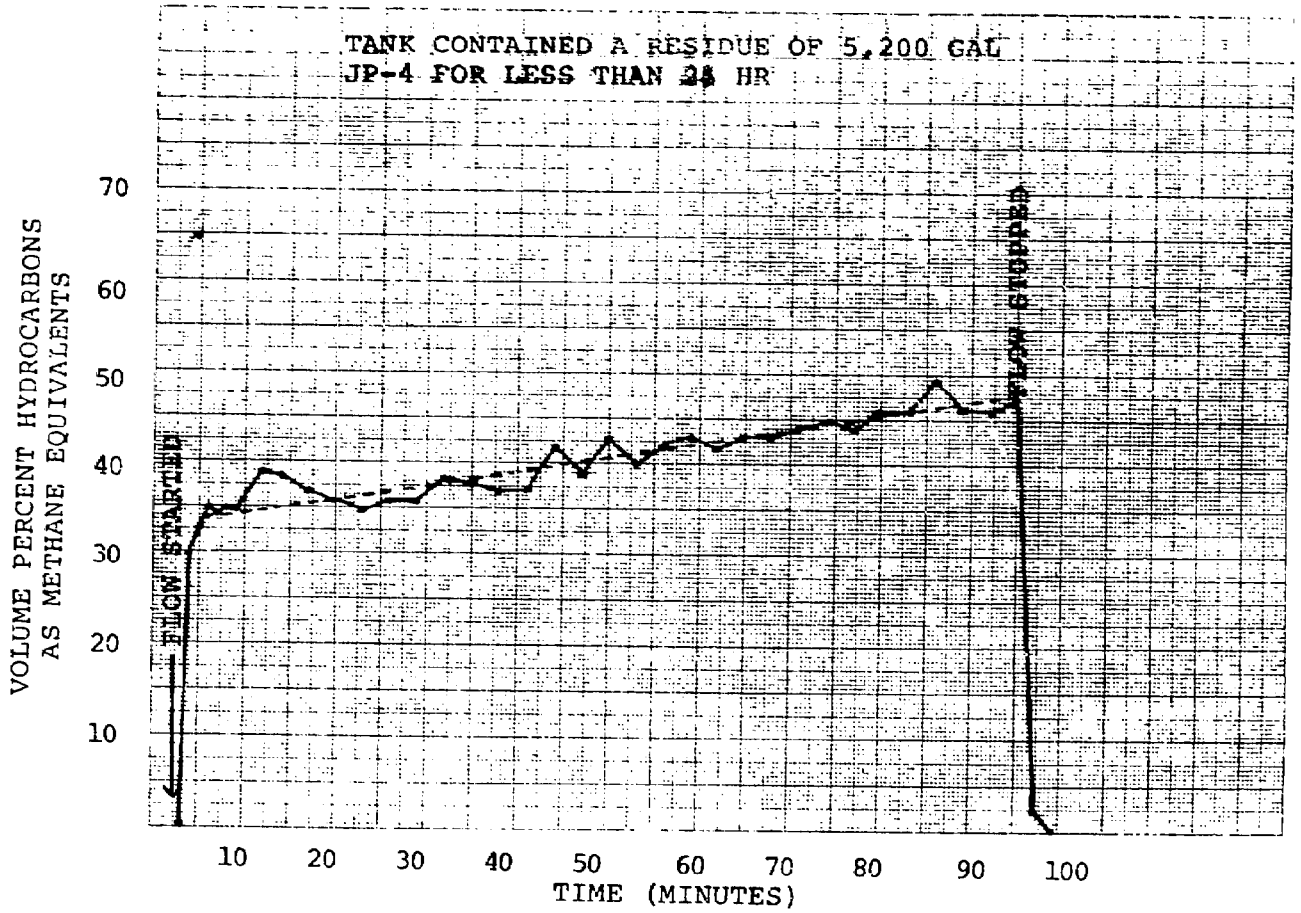


Figure 37. Hydrocarbon emissions from tank #285 during JP-4 fill operation.

of fuel delivered were extrapolated for each hydrocarbon data point using the fuel-delivery data illustrated in Figure 36. Hydrocarbon emission levels are observed to vary from approximately 45% to 57% during the fill of tank #283 while hydrocarbons from tank #285 range from 35% to 50%. As indicated in the previous section, Tank #285 contained an approximate 10% fuel residue which had been added less than 24 hours before measurements began. The difference in hydrocarbon emission levels from the two tanks is readily accounted for by this difference in the vapor/liquid equilibration periods. Cyclic variations in emission rates are observed for both tanks. These may result from changing wind patterns to which the vents are exposed or to surging of the fuel as it enters the tank. Irregularities are not caused by any variations in sample pumping rate since measurements are independent of sample flow rate providing the nitrogen blending ratio is unchanged.

Methane equivalents are commonly used for reporting volume concentrations of hydrocarbons. In order to obtain volume percent of a specific hydrocarbon, the methane equivalent value must be divided by the carbon number of the hydrocarbon or the average carbon number of the mixture. For pentane, a 50% methane equivalent is equal to 10% pentane.

Supplemental Fuel Data

A sample of the JP-4 pumped during the course of these tests was recovered and subjected to several quality control tests. These were conducted by Air Force Aero Propulsion Laboratory personnel. These data are presented in Table 51. The measured vapor pressure of 2.5 psi is midway between the specified 2-3 psi range. Distillation data characterize it as a typical JP-4.

TABLE 51. QUALITY CONTROL DATA FOR JP-4 FUEL USED IN TESTS

	Measured value[a]	Specification value
I. Distillation data		
Initial boiling point	143 (62)	-[b]
10% recovered, °F(°C)	195 (91)	-[b]
20% recovered, °F(°C)	217 (103)	293 (145) max temp
50% recovered, °F(°C)	275 (135)	374 (190) max temp
54% recovered, °F(°C)	290 (143)	-[c]
83% recovered, °F(°C)	370 (188)	-[c]
90% recovered, °F(°C)	403 (206)	473 (245) max temp
End Point recovered, °F(°C)	474 (246)	518 (270) max temp
II. Vapor pressure, 100°F	2.5 psi	2.0 - 3.0 psi
III. Fuel system icing inhibitor, volume %	0.09	0.10 - .15

a Measurements conducted by APAPL personnel
b Not limited, to be reported
c Not specified

2. COOPERATIVE EVALUATION OF PROPOSED ANALYTICAL METHOD FOR JP-9 FUEL

JP-9 fuel consists of relatively few components compared to conventional fuels such as JP-4, JP-7 or JP-8. Fuel quality specifications, therefore, can be established for JP-9 primarily on the basis of its chemical composition. Work was conducted in a cooperative program for evaluating an analytical method for JP-9 proposed by Dr. R. D. Butler of the Air Force Aero Propulsion Laboratory. The method requires the use of gas chromatography to completely resolve and determine the three major blending stocks, methylcyclohexane (MCH), exo-tetrahydrodicyclopentadiene (exo-THD) and hydrogenated norbornadiene dimer (RJ-5). Response factors are determined and applied to give the fuel composition in true weight percent.

Procedure

A Perkin-Elmer Model 3920-B gas chromatograph, having a 50-meter glass open-tubular column coated with SF-96, was used for the evaluation. Resolution, defined as the difference in retention times for C_{12} and C_{14} alkanes divided by the average peak width, was calculated to be 41.5 (Figure 38).

Complete instrument conditions are presented below.

Instrument	Perkin-Elmer Model 3920B
Column: Stationary Phase	SF-96
Length	50 meters (glass)
Diameter	0.01 inch
Detector Type	Flame Ionization
Carrier Gas	Nitrogen
Flow Rate	3 ml/min

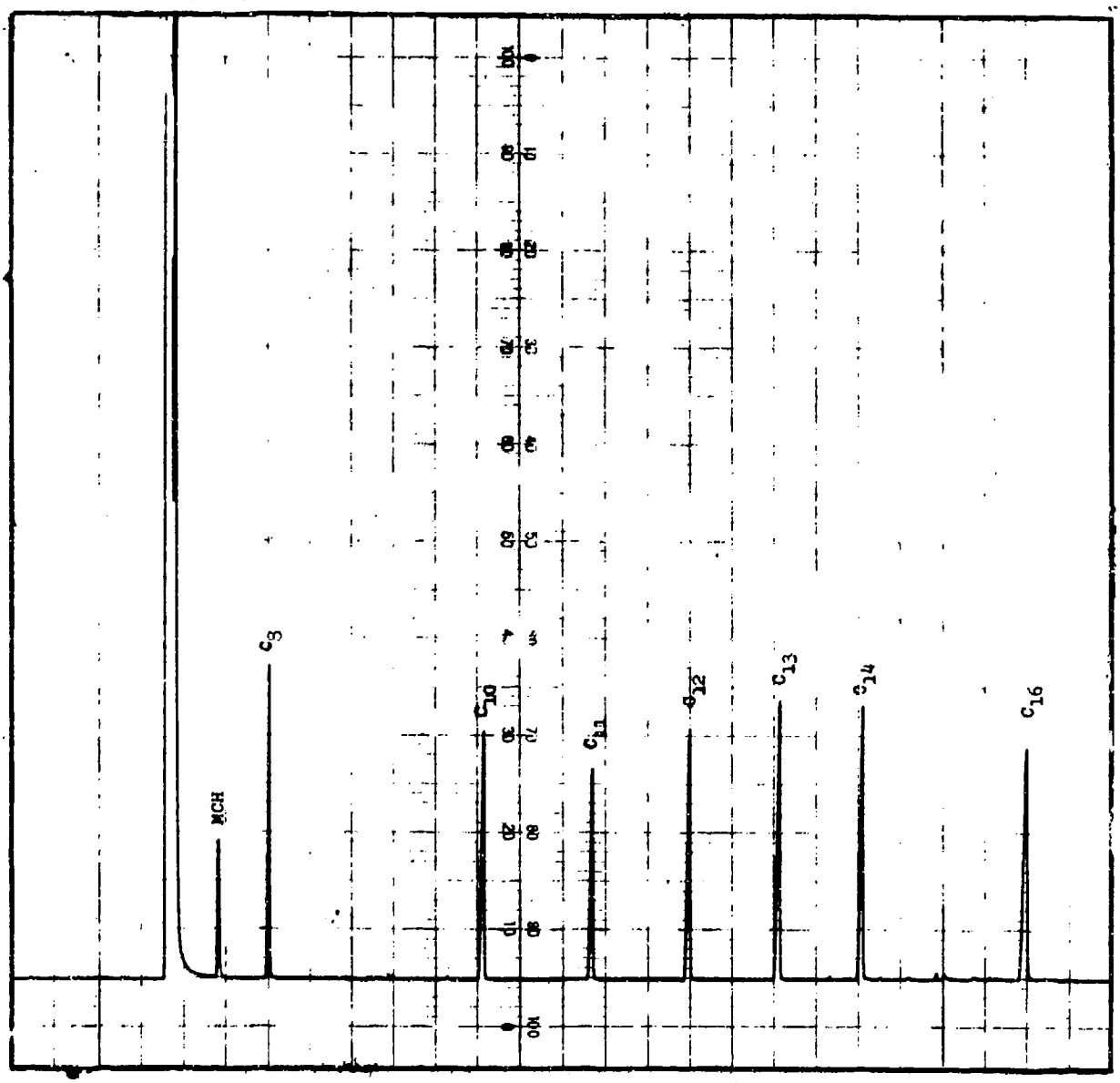


Figure 38. Chromatogram of n-alkane mixture, showing suitable resolution based on C_{12}/C_{14} separation.

Temperature Program:	60°C
Initial Temperature	4 min
Initial Hold Period	4 min
Program Rate	4 °C/min
Final Temperature	180°C
Injection Port Temperature	300°C
Detector Temperature	300°C
Integrator	Hewlett-Packard Model 3380A
Sample Volume	0.5 µl (split 100:1)
Sample Dilution	1:40 (n-Pentane)
Cycle Time	40 min

Standard blends were prepared by weight using MCH, exo-THD from 3 different batches, and RJ-5 from 4 different batches. The compositions of these standards are presented in Table 52. Each of the six standards was diluted 40-fold with pentane and chromatographed three or more times injecting approximately one-half microliter of sample each time. Response factors for exo-THD and RJ-5 were calculated relative to MCH which was assumed to have a response factor of 1.000. Average response factors for each standard and the grand mean value for each component are presented in Table 52. It is noteworthy that the RJ-5 response factors are relatively uniform for all batches of that material. A small but significant difference, however, can be observed between the responses of monoisomeric and polyisomeric THD.

Results

Fuel samples to be analyzed were obtained from the Air Force Aero Propulsion Laboratory. The samples were diluted and analyzed in the same manner as the standard blends, each sample being analyzed at least five times. The previously determined response factors were applied to compute compositions in weight percent. A typical chromatogram is presented in Figure 39.

TABLE 52. COMPUTATION OF RESPONSE FACTORS FOR JP-9 COMPONENTS

Blend No.	Lot Designation[a] of Components exo-THD	RJ-5	Blended Composition, Weight % MCH	exo-THD	RJ-5	Determined Response Factor c exo-THD	RJ-5
1	C[b]	F	23.85	20.12	56.03	1.0107	0.7383
						0.9831	0.7686
						0.9396	0.7145
						0.9571	0.7429
					Average	0.9722	0.7410
2	A	D	28.73	18.56	52.71	0.8687	0.7266
						0.9173	0.7636
						0.9182	0.7546
						0.9012	0.7567
					Average	0.9015	0.7504
3	B	E	23.77	14.69	61.54	0.8881	0.7194
						0.8983	0.7315
						0.8797	0.7426
						0.8887	0.7378
4	B	E	30.50	11.13	58.37	0.9123	0.7520
						0.8877	0.7150
						0.9023	0.7500
						0.9008	0.7389
5	A	D	21.04	16.78	62.68	0.9300	0.7752
						0.8902	0.7415
						0.8690	0.7327
						0.8964	0.7495
6	C[b]	G	42.01	9.71	48.28	1.0229	0.7324
						0.9768	0.7515
						1.0062	0.7452
						1.0020	0.7430
					Grand Mean	0.9269	0.7434

[a] Components from diverse sources were used to establish the general validity of the procedure.

[b] Polyisomeric THD

[c] Relative to a response factor of 1.0000 for MCH.

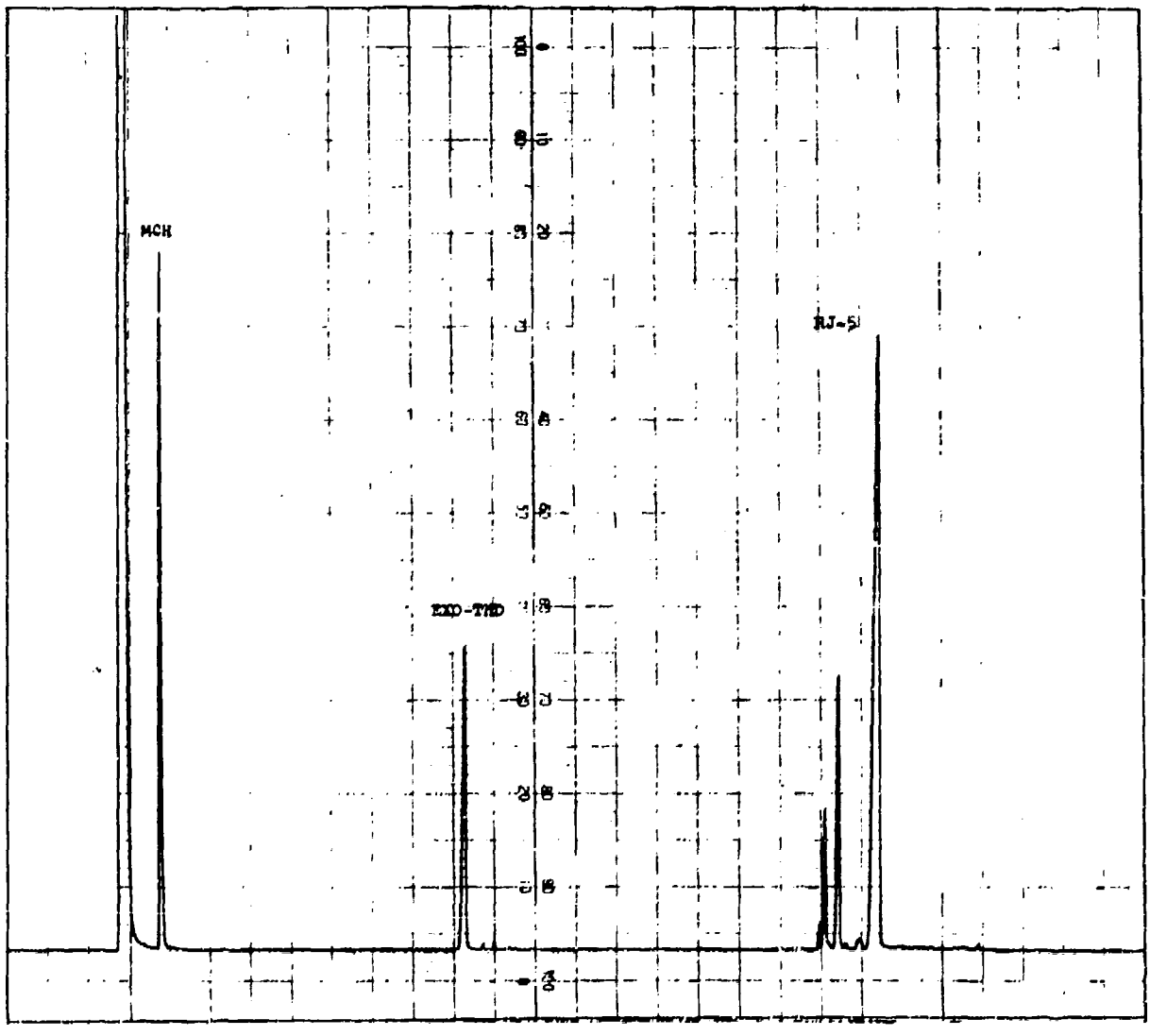


Figure 39. Chromatograph of JP-9 sample #18.

Samples were also analyzed at the Air Force Aero Propulsion Laboratory, though results of those analyses and the true blending values were not revealed until completion of the study. Data are compared in Table 53.

The excellent agreement of the results from the two laboratories with the true blending values confirms the usefulness of the method for the rapid and routine measurement of JP-9 fuel composition. The method has subsequently become a part of Military Specification Mil-P-87107, "High Density Synthetic Hydrocarbon Type Propellent, Grades JP-9 and JP-10," issued July 1977.

Heat of Combustion Measurements on JP-9 Test Samples

In conjunction with the analytical method evaluation, net heat of combustion values were determined for each of the blending components used for preparing standards, as well as each analyzed fuel blend.

An oxygen bomb calorimeter was used exactly as described in ASTM D240-64. Method D240 gives two separate equations for calculating net heat of combustion from the gross value. The equation:

$$H_n = H_g - 91.23H \quad (4)$$

where H_n = net heat of combustion (BTU/lb)
H_g = gross heat of combustion (BTU/lb)
H = percent hydrogen in the sample

is preferred when the hydrogen content of the fuel is known. If this value is not available, the net heat of combustion can be calculated by equation:

$$H_n = 4310 + (0.7195)\ H_g \quad (5)$$

TABLE 53. RESULTS OF COOPERATIVE EVALUATION OF JP-9 ANALYTICAL METHOD

Sample Number	Component	Weight Percent, Five Analyses							Mean Value	AFAPL[a] Analysis	True[b] Value
18	MCH	21.27	21.18	21.50	20.71	21.15			21.16	21.40	21.74
	exo-THD	14.29	14.38	14.34	14.27	14.22			14.30	14.29	14.28
	RJ-5	64.44	64.44	64.16	65.01	64.63			64.53	64.31	63.97
21	MCH	36.49	37.11	36.87	36.57	36.81			36.77	37.00	37.37
	exo-THD	13.28	13.21	13.42	13.28	13.33			13.30	12.97	13.08
	RJ-5	50.23	49.68	49.71	50.15	49.86			49.93	50.04	49.55
38	MCH	22.64	23.11	22.05	22.86	23.04			22.74	22.78	23.08
	exo-THD	20.12	20.58	20.18	20.32	19.82			20.20	19.92	19.88
	RJ-5	57.24	56.31	57.77	56.82	57.14			57.06	57.30	57.03
50	MCH	33.85	33.21	33.23	34.08	33.15			33.50	33.48	34.83
	exo-THD	11.65	11.79	11.76	11.73	11.63			11.71	11.55	11.59
	RJ-5	54.49	55.00	55.01	54.19	55.22			54.78	54.97	53.59
51	MCH	22.49	23.07	22.92	23.43	23.27	23.15	23.06	23.06	23.27	24.16
	exo-THD	10.37	10.54	10.65	10.79	10.65	10.36	10.36	10.36	10.31	10.48
	RJ-5	67.14	66.39	66.43	65.78	66.08	66.36	66.36	66.36	66.42	65.36

[a] Conducted by Dr. R. D. Butler, AFAPL; Mean Value from 15 determinations

[b] Based on component weights used for each blend

A previous investigation showed that the equations gave similar values for most JP-9 specimens. Net heats of combustion have been calculated in both ways using the theoretical values for hydrogen in MCH, exo-THD, and RJ-5. These are:

Methylcyclohexane, C_7H_{14}	14.37 hydrogen
Exo-THD, $C_{10}H_{16}$	11.84 hydrogen
RJ-5, $C_{14}H_{20}$	10.71 hydrogen

Account was not taken of the relative distribution of pentacyclic and hexacyclic dimers in calculating the percent hydrogen in RJ-5. The hydrogen content of the fuels was calculated using these values and the analyses presented in Table 53. All heat of combustion data are presented in Table 54.

3. HEAT OF FUSION MEASUREMENTS ON ISOMERS OF HYDROGENATED NORBORNADIENE DIMER

Heat of fusion values were measured for various isomers of hydrogenated norbornadiene (NBD) dimer. Enthalpies of fusion and melting temperatures are required for the calculation of phase diagrams of the pure materials. This work involved the gas chromatographic purification of the isomers and the measurement of their calorimetric properties by differential scanning calorimetry (DSC).

Purification of Isomers

Heat of fusion values have been previously measured for NBD dimers using specimens ranging from 97-99% in purity. In this work, an effort was made to exceed these purities in order to improve the melting characteristics of the specimens.

TABLE 54. HEAT OF COMBUSTION OF JP-9 COMPONENTS AND BLENDS

Sample	Gross, BTU/lb	Net, BTU/lb Equation 1[a]	Net, BTU/lb Equation 2[b]	Theoretical hydrogen content wt. %[c]
#18	18923			
	18970			
	av. 18947	17942	17892	11.56
#21	18907			
	1888			
	av. 18893	17903	17787	12.12
#38	18873			
	18904			
	av. 18891	17902	17824	11.69
#50	18833			
	18806			
	av. 18820	17851	17720	11.99
#51	18792			
	18797			
	av. 18795	17834	17739	11.57
exo-THD Batch A	19084			
	19094			
	av. 19089	18044	18016	11.76
exo-THD Batch B	19192			
	19169			
	av. 19185	18114	18112	11.76
exo-THD Batch C	19322			
	19333			
	av. 19328	18216	18255	11.76
RJ-5 Batch D	18791			
	18789			
	av. 18790	17829	17819	10.64
RJ-5 Batch E	18747			
	18738			
	av. 18743	17795	17772	10.64
RJ-5 Batch F	18743			
	18736			
	av. 18740	17793	17769	10.64
RJ-5 Batch G	18754			
	18780			
	av. 18767	17813	17796	10.64
MCH	19968			
	20008			
	av. 19989	18692	18700	14.28

[a]Calculated by equation based on the empirical relation between heat of combustion and hydrogen content in Aviation Turbine Fuels.

[b]Calculated by equation using exact hydrogen content of fuel.

[c]Used for calculations by equation 2.

NBD dimer isomers were purified by preparative gas chromatography. Since only milligrams of material were required for DSC measurements, sufficient sample was readily obtained using 0.25" O.D. columns. Fractions were collected using either of the two columns:

(a) 10% OV 225 on Chromosorb HP, 1/4" x 50'
(b) 3% Dexsil 300 on Chromosorb HP, 1/4" x 50'

The OV 225 column provided good separation of isomers but it was suspected of causing impurities by column liquid-phase bleed. The Dexsil 300 column was substituted to eliminate this source of possible contamination.

Initially, fractions were collected from RJ-5 fuel samples. However, work was soon concentrated on purifying existing fractions of known isomers. All fractions were assayed by high resolution gas chromatography using a 50-meter glass capillary column coated with SF-96. The measured purities of NBD dimer isomers used for heat of fusion calculations are tabulated in the last column of Table 55. The starting materials for most of these fractions were individual isomers of reasonably good purity which originated from Sun Oil Company. Though the purity was improved somewhat by preparative gas chromatography, the remaining small amounts of impurities were significant.

Calorimetric Measurements

A Perkin-Elmer DSC-1 Differential Scanning Calorimeter was used to examine the melt behavior of the NBD dimer isomers. Indium metal, 99.9999% pure and melting at 429.7°K, was used for temperature and heat calibration. Samples in the milligram range were used and were hermetically sealed in aluminum pans to prevent loss of volatiles. Temperatures were lowered slowly in order to reduce the possibility of super cooling or glass formation. Data

TABLE 55. MELT DATA FOR ISOMERS OF HYDROGENATED NORBORNADIENE DIMER

Isomer	Sample weight, mg	ΔH_f cal/g	Premelt corr. factor	To (°K)	ΔH_f (corrected) K cal/mol	Purity by gas chromatography
Exo-t-Exo pentacyclic dimer	5.95	8.38	0.27	336.8	2.00	99.3
		9.67[a]	0.18	337.5	2.15	
Exo-endo hexacyclic dimer	6.85	6.75	0.28	294.5	1.61	98.4
Exo-exo hexacyclic dimer	10.15	15.2	0.21	285.5	3.19	99.0
Endo-endo hexacyclic dimer	7.90	16.9	0.10	282.9	3.46	98.5

[a]Not a replicate determination, but a different sample.

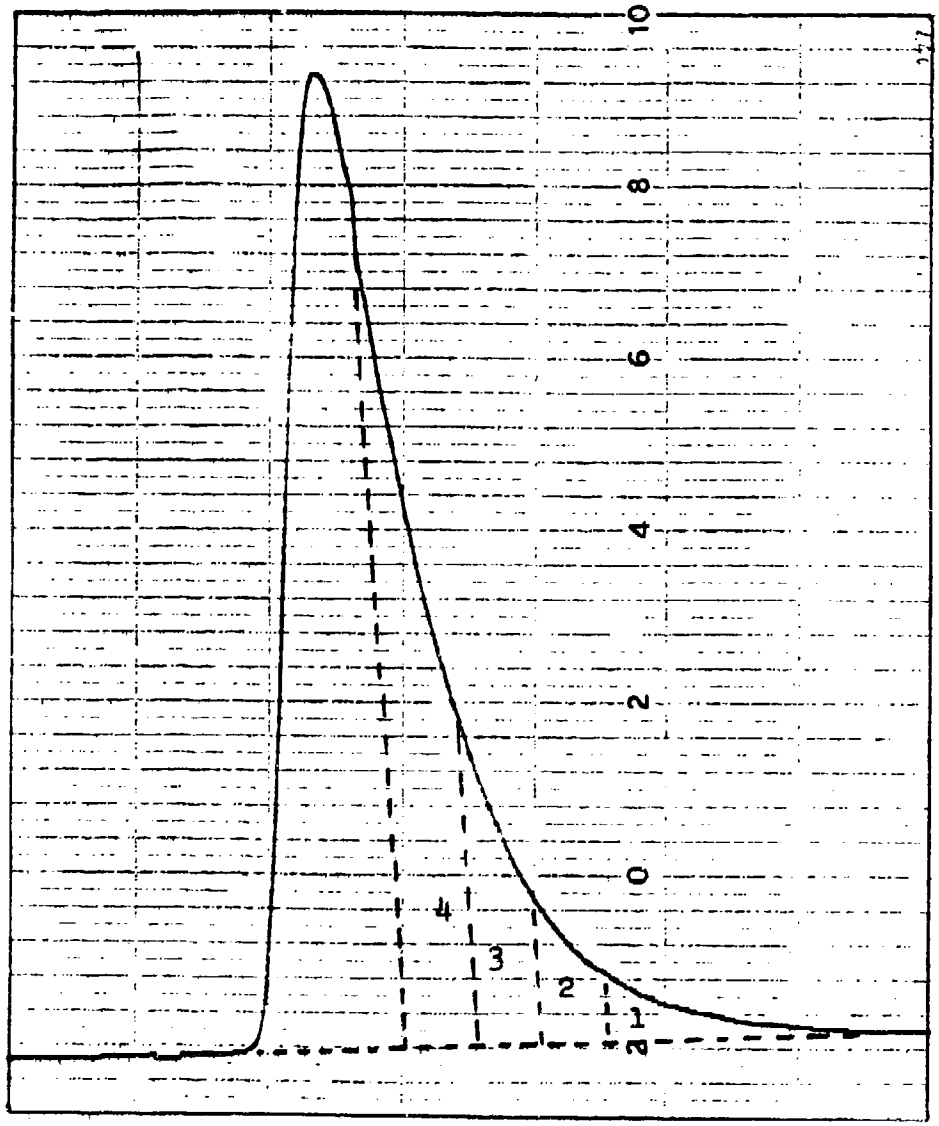
were recorded during the cooling cycle in order to observe the crystallization exotherm. A heating rate of 1.25 degrees per minute was used for all measurements.

Results and Discussion

Since a DSC peak is a plot of heat (millicalories) lost or gained by the sample versus its temperature, the area under the DSC curve can be directly related to the heat of fusion of the sample. The amount of heat absorbed is directly proportional to the amount of sample melted and to the amount of area shown on the chart. Consequently, the fraction of the sample melted at any temperature is equal to the fraction of the total peak area below that temperature. The reciprocal of the fraction melted (1/F) is directly proportional to the temperature, T. For very pure samples, a plot of 1/F versus T is linear. The presence of even small amounts of impurities causes the melting range to broaden and a plot of 1/F versus T is concave upward. A correction for premelting is required and is applied so that the 1/F vs T plot is linearized. This correction, which is illustrated in Figures 40 and 41, was calculated for all samples.

The melt temperature of each pure isomer, T_o, was obtained from a curve similar to that of Figure 41, and is equal to the zero intercept. As the chief purpose of these experiments was the determination of ΔH_f values, for which absolute temperature measurements are not required, only one temperature calibration standard was used. For highly accurate temperature measurements, a series of compounds melting over the complete range of interest should be used for calibration.

The exo-t-exo pentacyclic dimer exhibited two endotherms and these are shown by all samples of that isomer including those isolated from Shelldyne-H. The first peak was observed at nominally 322°K and second at 337°K. Though the additional peak may



Fraction	Integrated Area	1/F	Temperature °K
1	250	21	280.65
2	290	9.8	281.25
3	665	4.4	281.90
4	1900	1.7	282.50
Total	5300		

Figure 40. Melt curve for endo-endo hexacyclic dimer of NBD showing fraction of sample melted as a function of temperature.

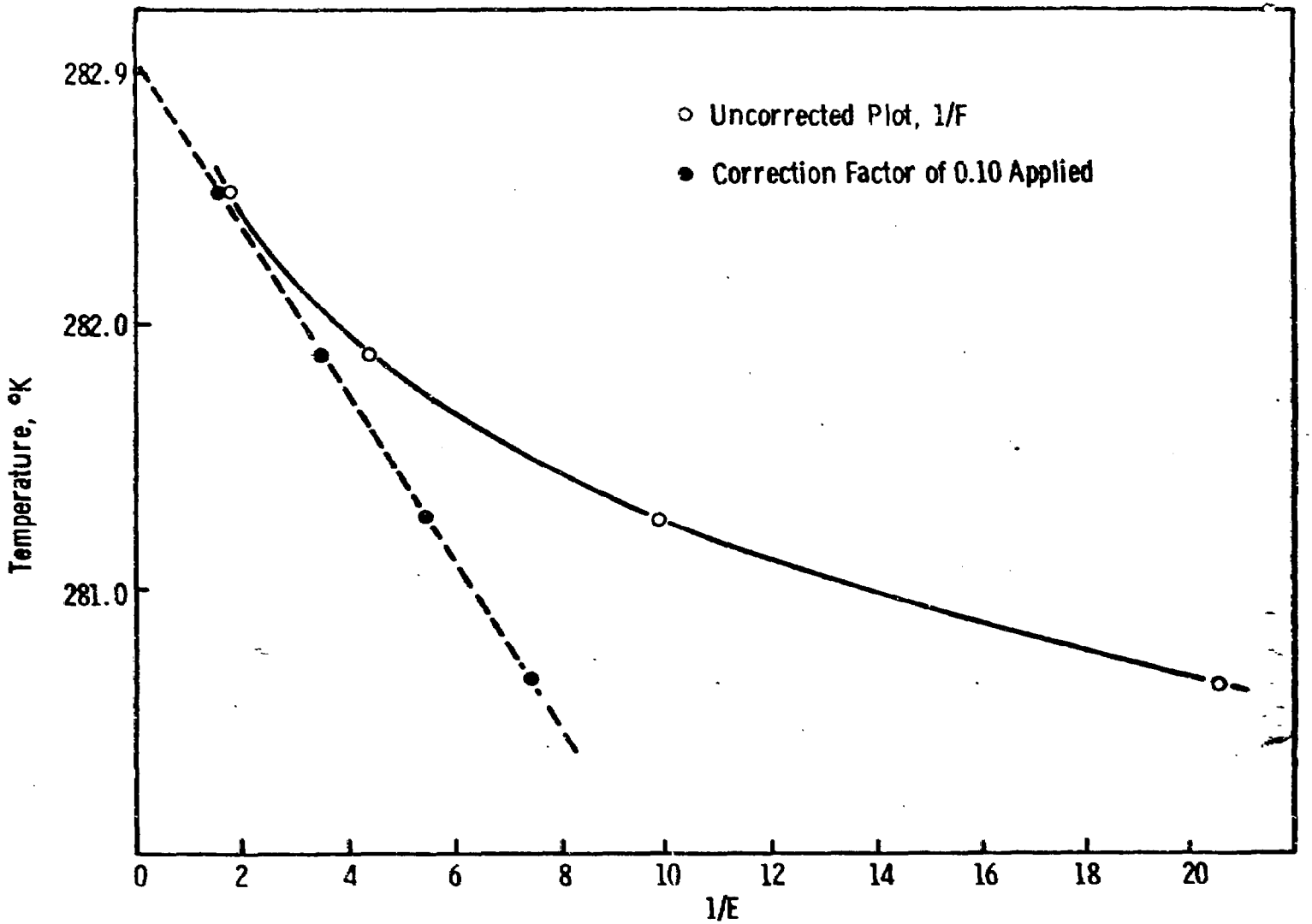


Figure 41. Plot of reciprocal of fraction melted vs temperature, with application of premelt correction.

be due to a second component, the relative sharpness of the peaks suggests a reasonably pure material, as is also shown by gas chromatography. The peak observed at the lower temperature is believed to be a solid-solid transition of the type common to some types of hydrocarbons. Dotriacontane, for example, shows a solid-solid transition at 338°K in addition to the melting transition at 343°K. In that case, the first transition represents the onset of a cooperative rotational mobility within the crystal.

Heat of fusion computations for the exo-t-exo pentacyclic dimer are based on the second peak which is completely resolved from the first. Data for all samples with premelt corrections are presented in Table 55. It should be noted that initial measurements on the exo-exo hexacyclic dimer showed a great deviation from expected results. Subsequent examination of the specimen showed it had been contaminated. The curve and data presented herein for that material was generated with a fresh portion of sample. The fact that the curve for this material is the reverse (mirror image) of the others has no significance. Melt curves are presented in Figures 40, 42, 43 and 44.

The greatest problem encountered in obtaining DSC data is in assuring complete crystallization upon cooling. One indication of incomplete crystallization is an unusually high premelt correction factor.

Impurities whose molecules are the same size and shape as those of the major component may be able to fit into the crystal without distorting the lattice, thus giving a solid solution not detectable by DSC.

The premelt correction is essential because the presence of even minute amounts of impurity or of crystalline defects broadens

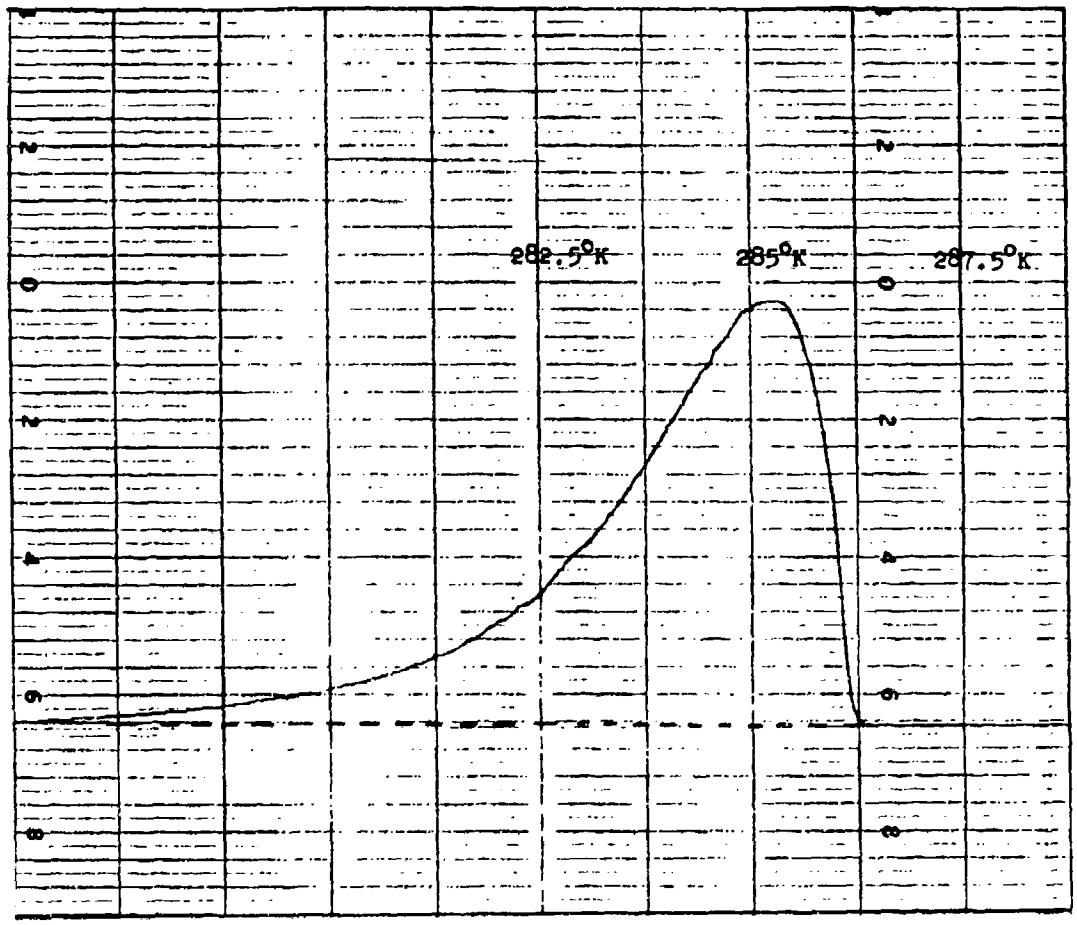


Figure 42. Melt curve for exo-exo hexacyclic dimer of NBD.

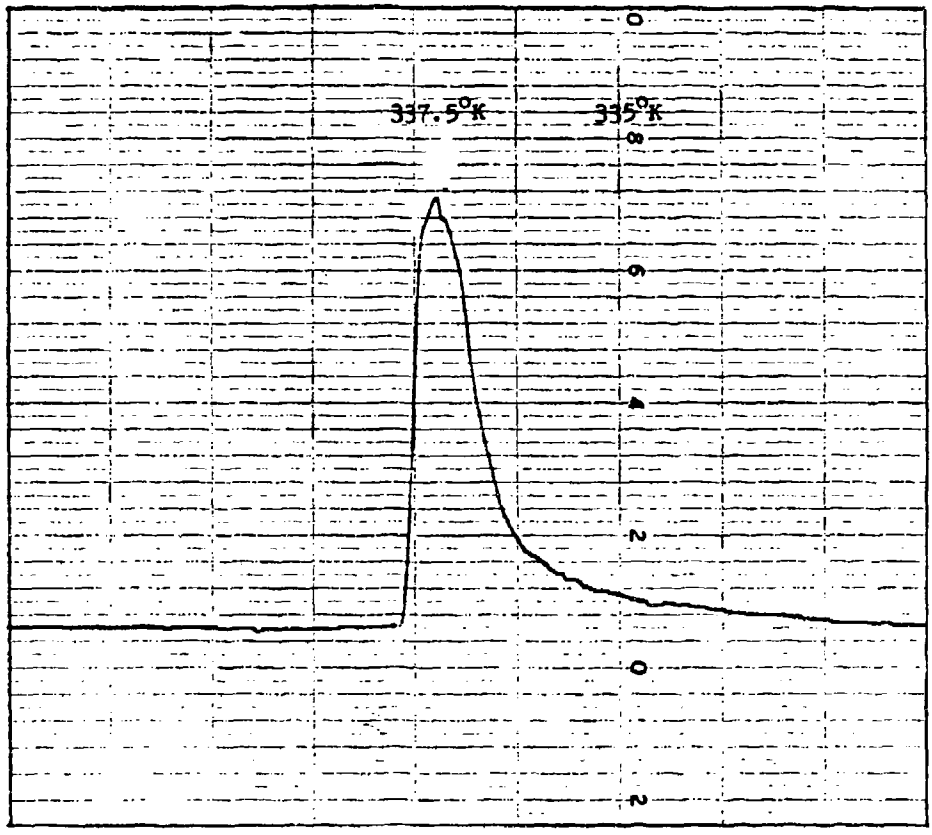


Figure 43. Melt curve for exo-t-exo pentacyclic dimer of NBD.

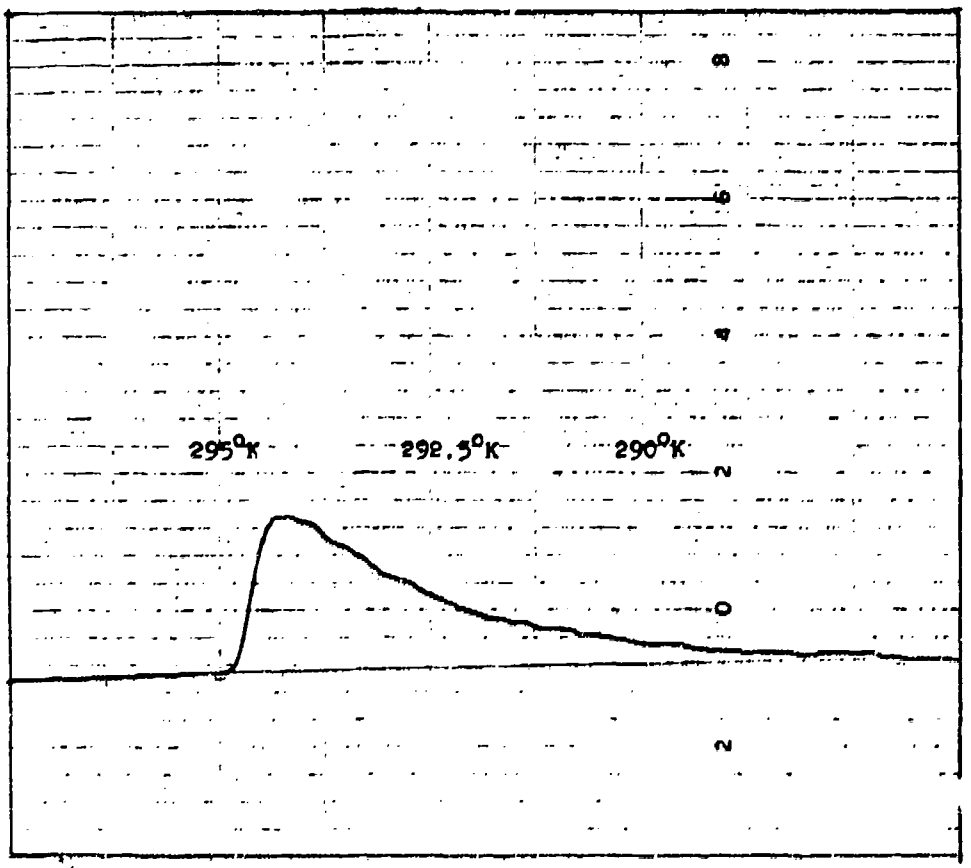


Figure 44. Melt curve for exo-endo hexacyclic dimer of NBD.

the melting range and lowers the final melting point. Consequently, a signficant portion of the specimen has melted before the melting curve rises above the baseline. It is unlikely that the NBD dimer isomers can be sufficiently freed of impurities so as to make this correction unnecessary. However, good values for the heat of fusion should be obtained, even from impure samples, if the melting curve is analyzed and the 1/F plot linearized as described in the foregoing.

4. EVALUATION OF TYNDALL LIGHT SCATTERING FOR DETECTING FUEL ADDITIVE INCOMPATIBILITY

The anticipated use of a new antistatic additive in aircraft fuels requires a careful evaluation of the additive's compatibility with each of the large number of other additives already contained by or approved for use in these fuels. Simple combinatorial analysis shows that the possible number of such compatibility tests could be extremely large, thus a simple and rapid means of detecting incompatibility is required. The probable form in which additive incompatibility would manifest itself is in the formation of suspended matter in the fuel. Tyndall light scattering measurements, or nephelometry, using a laboratory spectrophotofluorometer has been investigated as a rapid screening technique to detect suspended material in fuel specimens. The use of a spectrofluorometer in nephelometry has been recommended (9) because of that instrument's inherent sensitivity.

Theoretical and Experimental

A true solution has little tendency to scatter light. However, a beam of radiation passing through a sample containing randomly dispersed inhomogeneities, produces scattering by the Tyndall effect. Rayleigh scattering, which arises from transitory fluctuations in the index of refraction of the medium, may also occur. In order to estimate the level of suspended matter using

Tyndall scattering, Rayleigh scattering, which is not directly related to the amount of suspended material, must be taken into account. Other optical phenomena which could potentially interfere with Tyndall scattering measurements are Raman scattering and fluorescence by the sample. Both of these effects, however, are associated with a shift in wavelength, i.e., they occur at wavelengths greater than that of the incident radiation.

An Aminco Bowman spectrophotofluorometer having a high pressure xenon source and a photomultiplier detector, was used for the work. With this instrument, samples may be irradiated with a monochromatic beam of any wavelength from 200 to 800 nm. Light which emerges at a 90° angle to the incident beam passes through a monochromator before being measured. A wavelength of 445 nm was selected for measurement, as the sample absorbs very little at that wavelength and consequently fluorescence is negligible. By making measurements at a wavelength exactly equal to that of the monochromatic incident beam, only Tyndall and Rayleigh effects were measured. To distinguish between the two types of scattering, it was necessary to filter through a Millipore® 0.45 micron filter (HAWP 047 00). Measurements conducted on each fuel after filtration were assumed to exhibit only Rayleigh scattering and the difference between the measurements taken before and after filtration gave the amount of Tyndall scatter. At the present time, scattering has not been quantitatively related to the suspended particulate content; such calibration would require suspensions of known particle concentration. The purpose of this work is to test the sensitivity of the Tyndall scattering method to determine if it might be used to indicate a level of particulate in the fuel above that which would result from normal handling and shipment.

Results

All fuels included in this study were free of any visual turbidity, though they were all pale yellow in color. Each fuel upon receipt contained fuel system icing inhibitor, the antistatic additive ASA3, and at least one other additive. The exception was a baseline JP-4 fuel which contained only icing inhibitor.

Scattering was measured by wavelength-scanning across the scatter peak of both the filtered and unfiltered fuel, with all measurements being conducted in triplicate. Figure 45 illustrates the scatter peak of Fuel P-2 before and after filtration. In this case the Tyndall and Rayleigh effects are approximately equivalent. Expressing Tyndall scattering in terms of percent of total scatter, however, has little significance since Rayleigh scattering may also vary from sample to sample. For this evaluation, Tyndall scattering values were normalized with a relative intensity of 100% being arbitrarily assigned to the sample having the greatest scatter.

Discussion

Measurements presented in Table 56 represent blind analyses in that no information was supplied concerning suspected or measured additive incompatibility or dispersed particulate content. The fact that, in all cases, filtering lowered overall scattering is encouraging and indicates a strong correlation between the particle content and scatter intensity. Another observation which provides consistency to the results is that the two samples having the greatest scatter have a common additive, HT-15, and these are the only samples to contain that material. The baseline JP-4, whose scatter was quite low, showed a small decrease in scatter after filtration. This indicates that some particulates may be introduced into the fuel through normal handling. The filtration step requires great care as a relatively small amount of fuel was

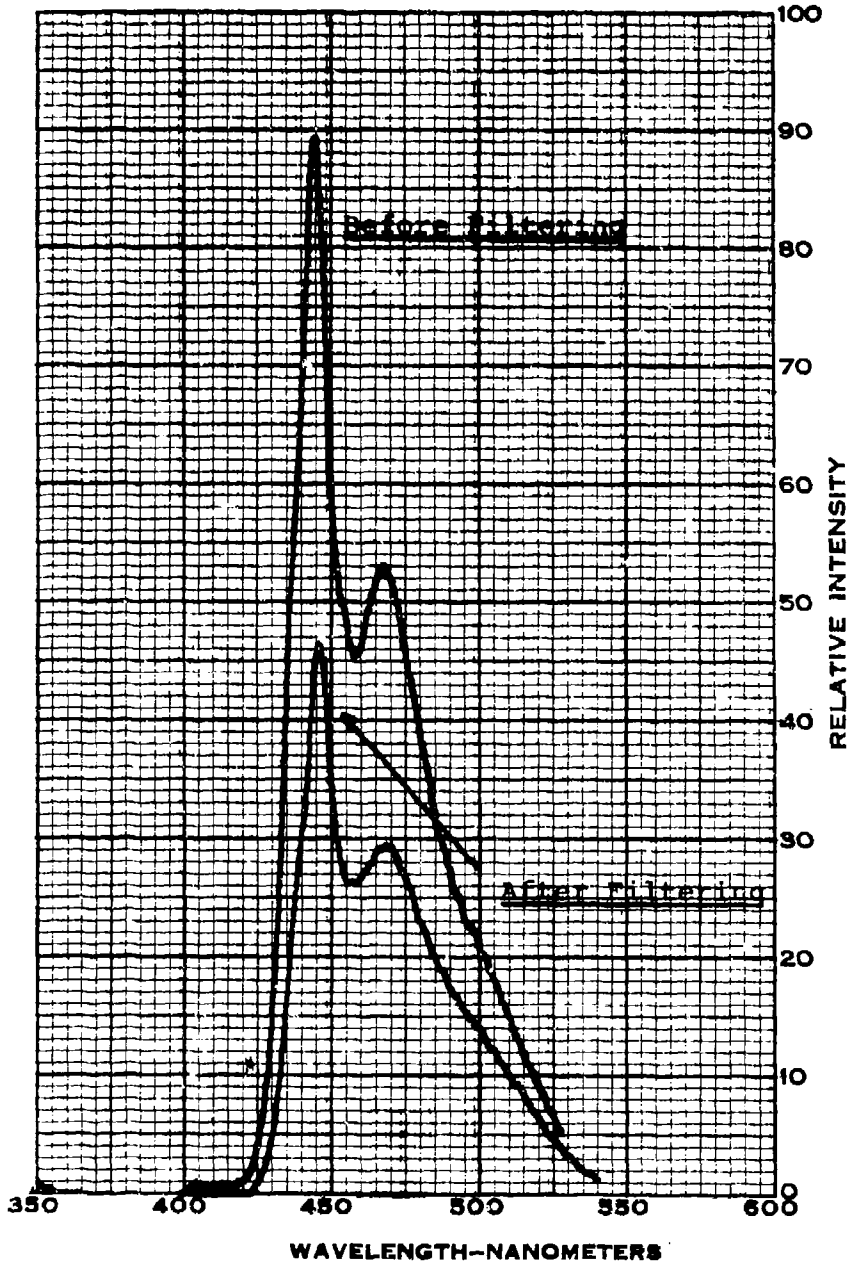


Figure 45. Scatter peaks for fuel P-2 before and after filtration.

TABLE 56. RELATIVE TYNDALL SCATTERING AND ADDITIVE CONTENT OF FUELS

Fuel Number	Relative Tyndall Scattering	Fuel Additives Contained									
		FS	S450	NC02	DC4	UNJ	HT15	AD23	AP-19	MD	ASA3
P-2	100	X					X				X
P-5	74	X	X				X		X		X
P-21	21	X			X						X
P-19	16	X				X		X		X	X
P-20	14	X		X							X
P-9	0	X						X			X
JP-4	5	X									X

filtered in each case; any small amount of contamination introduced could be significant. A filter having a mean pore size of 0.45 micron should be adequate, as this pore size will retain most non-living particles and many types of bacteria.

Examination of the filters after use showed that two fuels, P-9 and P-19, had caused a slight filter darkening. These fuels, however, did not show appreciable Tyndall scattering. Specimens of the two fuels were placed in ASTM Petroleum centrifuge tubes and rotated at 4500 rpm for 3 minutes. A small amount of dark material was removed from 100 ml of P-19 fuel by this procedure. No deposit from P-9 was noticed.

The foregoing observations do not seem to agree with results from scattering measurements. Apparently the particle size of the contaminant in fuels P-9 and P-19 is sufficiently large that the material is not suspended in the fuel. Tyndall scattering measurements, possibly followed by microscopic examination of the filter, may offer the best approach to this problem.

5. COMPARISON OF AN EXPERIMENTAL FUEL WITH OTHER FUELS

Gas chromatographic simulated distillations were conducted on six fuel specimens to compare the boiling range of an experimental fuel with those of five other fuels. The fuels included in the study were JP-4, JP-7, JP-8, Jet A, regular gasoline and the experimental fuel.

In the procedure, as described in ASTM D2887, a fuel is injected into a gas chromatographic column which separates hydrocarbons in the order of their boiling points. Recorded retention times are related to boiling points by means of a calibrating mixture of pure n-alkanes. Initial and final boiling points are defined as the points at which the cumulative area under the chromatographic curve equals 0.5% and 99.5%, respectively.

A Hewlett-Packard Model 5730-A chromatograph with a Model CRS-101 Infotronics integrator was used for this work. A 24" x 1/8" stainless steel column packed with 10% UC W98 on 80-100 mesh Chromosorb W, AW, was programmed from -50 to 270°C at 8°C/min for regular gasoline, JP-4 and Jet A. For the other fuels, the temperature was programmed from 25 to 270°C, also at 8°C/min. A flame ionization detector was used with helium as the carrier gas. Area measurements were automatically recorded at each 10-second interval during the chromatographic run. Individual area measurements were entered into a computer for calculation of total area, cumulative area at each 10-second interval and cumulative percent of total area at each interval. From these data, retention times corresponding to the initial boiling point and end point, as well as intermediate points, were readily determined. A series of n-paraffins ranging in carbon number from 3 to 18 were used for temperature/retention time calibration. Data for these hydrocarbons, under the two temperature programs are plotted in Figure 46.

A series of distillation points for each fuel are shown in Table 57. A comparison of boiling range distributions are graphically presented in Figures 47 and 48.

Conclusions

The boiling range distribution of the experimental fuel does not completely match that of any other fuel specimen. It appears, however, to most closely resemble Jet A in its boiling characteristics. Both have approximately the same initial boiling points, though the temperatures diverge somewhat through the boiling range of the two specimens. The spread is 24°C at 25% distilled, 33°C at 50% distilled and 35°C at the end points. The most unusual feature of the boiling range curve for the experimental fuel, however, is the absence of the typical "S" shown by the

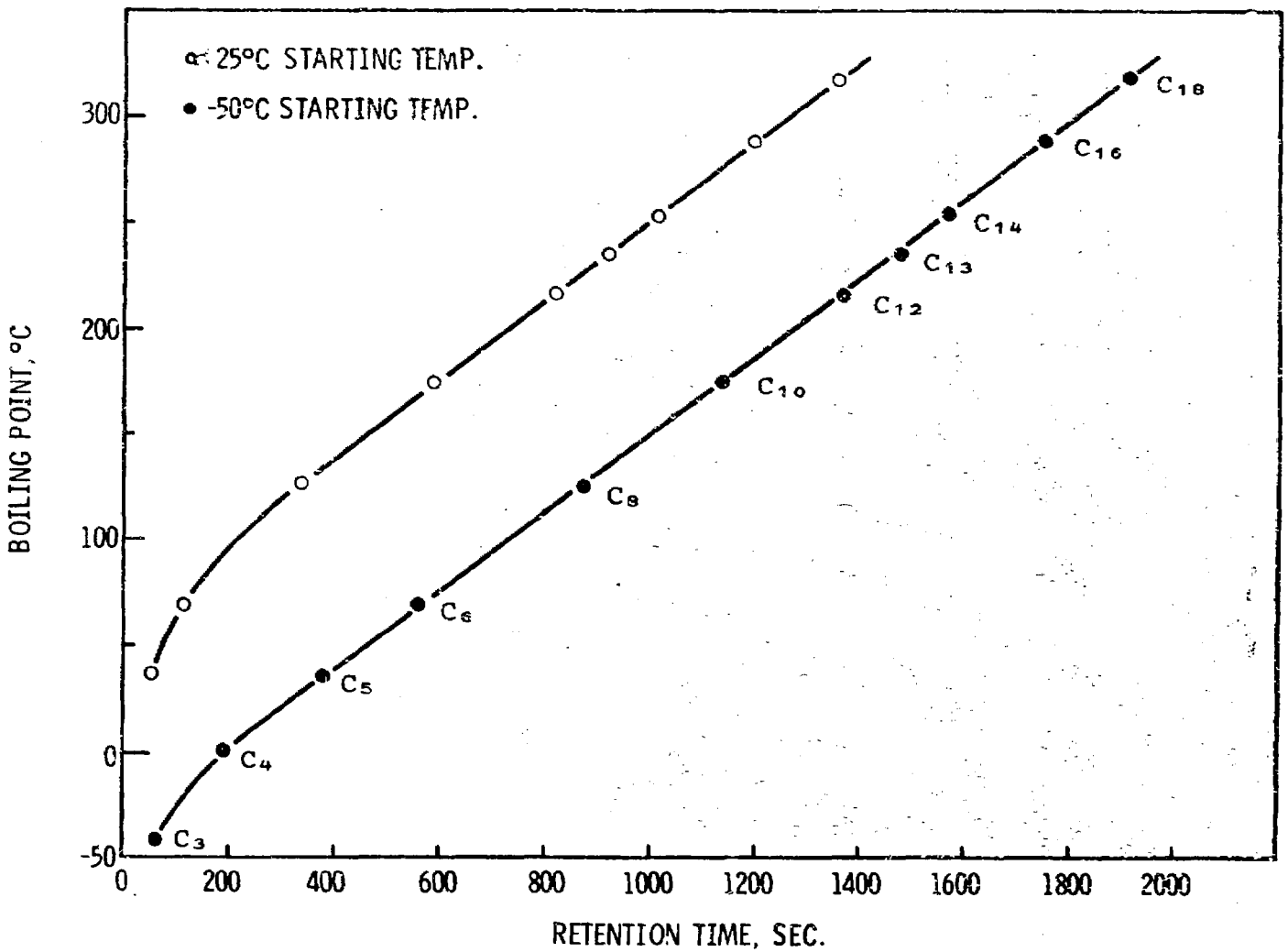


Figure 46. Boiling point calibration using n-alkanes from C_3-C_{18}.

TABLE 57. BOILING RANGE DISTRIBUTION DATA FOR SIX FUELS

	Temperature (°C)					
	JP-7	JP-8	Experimental fuel	JP-4	Jet A	Regular gasoline
IBP	123	30	75	-13	72	-15
1% distilled	133	67	92	0	88	-14
2% distilled	136	89	95	2	94	-13
3% distilled	140	93	102	9	101	-12
5% distilled	145	103	112	26	107	-3
7% distilled	148	107	119	33	118	0
10% distilled	151	115	138	45	124	3
15% distilled	158	123	155	64	136	24
20% distilled	165	136	168	78	147	34
25% distilled	172	145	180	91	156	45
35% distilled	185	166	201	112	172	70
50% distilled	204	192	229	145	196	108
65% distilled	222	218	256	182	218	146
75% distilled	235	235	276	206	234	173
85% distilled	248	254	300	232	251	202
90% distilled	255	264	313	246	262	217
93% distilled	260	271	322	254	269	229
95% distilled	264	276	328	261	276	236
97% distilled	268	283	336	268	285	247
98% distilled	270	287	341	272	292	253
99% distilled	273	293	348	278	302	268
FBP	277	304	358	287	323	319

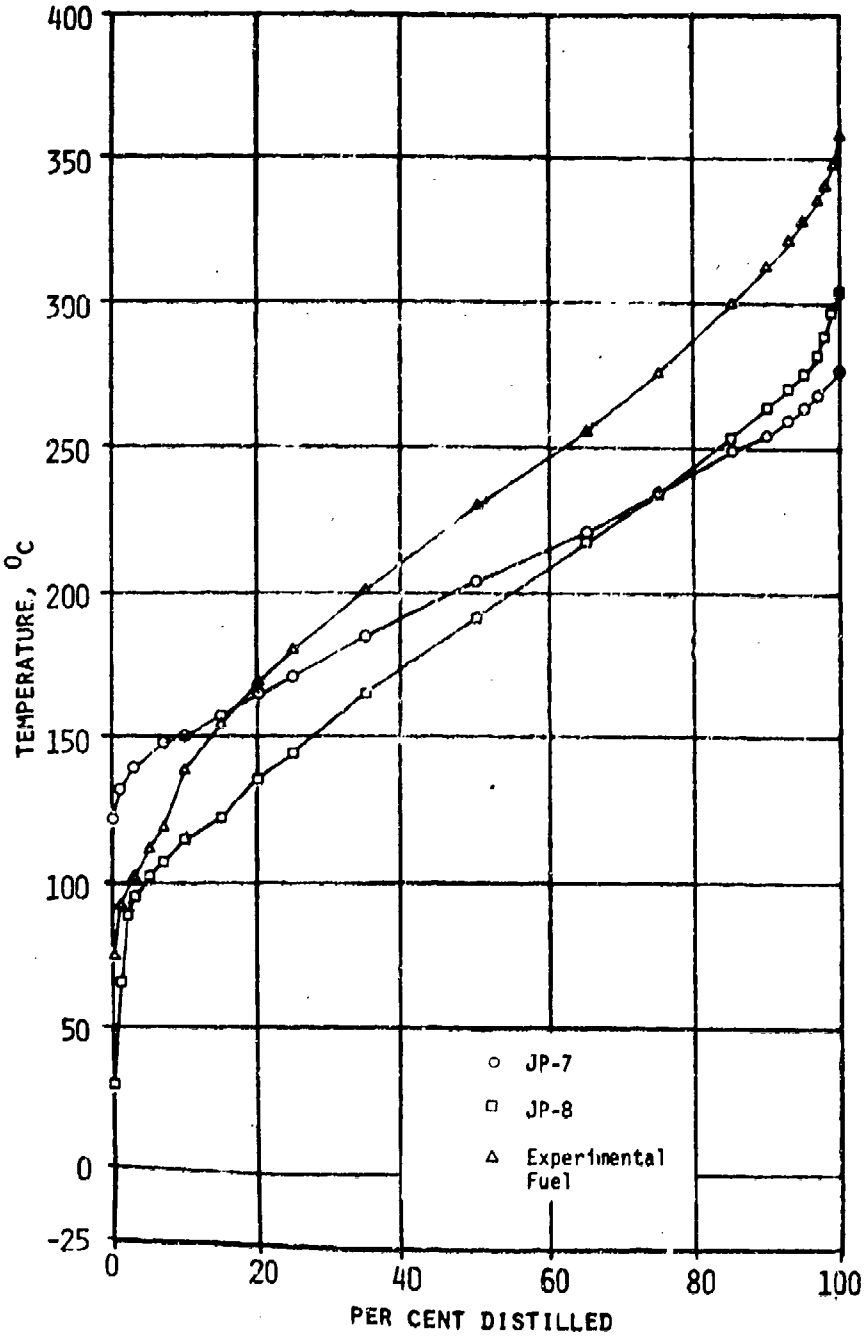


Figure 47. Comparison of boiling point distribution of three fuels.

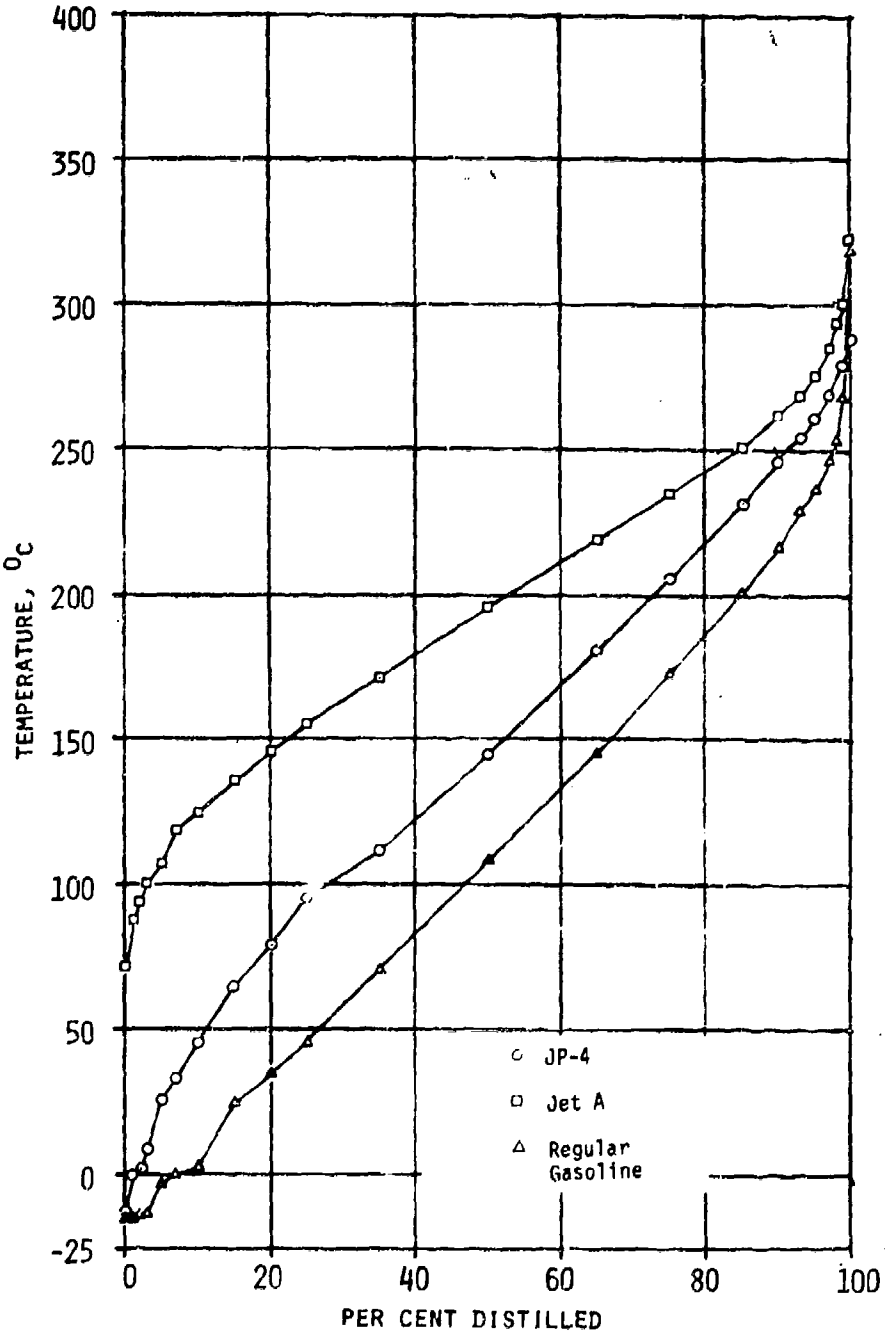


Figure 48. Comparison of boiling point distribution of three fuels.

curves of the other fuels. The boiling point curve of the experimental fuel approaches linearity from 15% distilled to the end point. The only other curve showing this trend is the curve of JP-7 and that fuel, of course, has a very narrow boiling range.

6. INVESTIGATION OF A CANDIDATE NON-HAZARDOUS CALIBRATING FLUID

An aircraft fuel system calibrating fluid similar to test fluid Mil-F-7024B, Type II, but having a low flash-point or being non-flammable, is urgently needed. Such a fluid for use in aircraft engine test facilities would greatly improve safety of operations and substantially lower the construction costs of the test facilities.

Tests were conducted on two candidate non-hazardous calibrating fluids as part of an investigation to identify a low-flammability replacement for calibrating fluid Mil-F-7024B. The fluid of primary interest was a blend of Freon®-TF (81.8% by weight) and Suniso®-3GS oil (18.2% by weight). Properties evaluated include specific gravity, viscosity, compatibility with elastomer seals, evaporation loss and lubricity. Other fluids included in parts of the investigation are the present calibrating fluid Mil-F-7024B, Exxon Fluid FN 3146, and the FN 3146 blended with Freon-TF.

Viscosity and Specific Gravity

The specific gravity of the Suniso 3GS/Freon-TF blend was determined by the pycnometer method. Viscosity was determined by a procedure essentially as described in ASTM Method D445. A blend of Exxon FN 3146 and Freon-TF, having a viscosity of one centistoke was prepared. Equal volumes of the two fluids were found to yield a blend having a viscosity of 1.04 centistokes. This blend has a Freon-TF/FN 3146 ratio of 1.865:1 on a weight basis. The approximate density of Freon-TF was determined to be 1.56, and that of Exxon FN 3146 to be 0.835, both at 25°C. Specific gravities and viscosities of the fluid blends are presented in Table 58.

TABLE 58. VISCOSITY AND SPECIFIC GRAVITY OF FREON-TF/OIL BLENDS

Blend	Viscosity at 77°F (25°C) (centistokes)	Specific Gravity at 77°F (25°C)
Suniso 3GS/Freon-TF 18.2%, 81.8% by wt.	0.991	1.3823
Exxon FN 3146/Freon-TF 34.9%, 65.1% by wt.	1.04	1.2005

Seal Compatibility

To test the compatibility of the Freon-TF/Suniso oil blend with various test stand seal components, elastomer sections were immersed in that fluid for periods of seven and forty-five days. Two sections of nominally 100 mm length of Buna-N and Viton-A O-rings were carefully weighed and measured before being placed in specimens of the fluid. Similarly, a specimen of a metal-reinforced braided fuel hose was cut into two pieces of nominally 50 mm length, with each being weighed and measured prior to being placed in fluid specimens. All samples were stored at 25°C with no further agitation. At the end of the storage period each sample was removed from the test solution and dried by gentle wiping until there was no visible indication of fluid. Weights and dimension were again carefully recorded. Initial and final weights and dimensions are presented in Table 59.

Visual examination of specimens, even those from the 45-day test showed no deformation or other ill-effects from contact with the fluid. Examination of the data in Table 59 shows that only in the case of the fuel hose was there significant weight gain. That particular specimen, due to its fabrication in layers of elastomer, cord and metal reinforcing, gave an abundance of interior spaces where the fluid could be physically entrapped. The weight gain is attributed to that phenomenon rather than to reaction of the fluid with the material. It will be noted that for all materials, swelling is minimal.

TABLE 59. COMPATIBILITY OF SEAL COMPONENTS WITH SUNISO 3GS OIL/FREON TF BLEND

Test stand component or material	Length of test, days	Before contact		After contact		Comments
		Length, dia., mm	Weight, g	Length, dia., mm	Weight, g	
BUNA-N RUBBER	7	100 x 5.35	2.9369	100 x 5.35	2.9544	No observable swelling; 0.6% wt gain.
	45	100 x 5.35	2.9076	100 x 5.35	3.0051	No observable swelling; 3.3% wt gain.
VITON-A	7	100 x 2.58	1.0173	103 x 2.64	1.0705	3% swelling; 5.2% wt gain.
	45	100 x 2.58	0.9978	103 x 2.75	1.1065	3% swelling; 11.1% wt gain.
HOSE, braided metal reinforced	7	50 x 19.48	18.3562	50 x 19.62	19.7887	Swelling; length, none observed; dia. 1%; 7.7% wt gain.
	45	51 x 19.48	19.0877	52 x 20.59	20.7120	Swelling; length 2%; dia. 2%; 8.78 wt gain.

Evaporation Loss

Information was required on the open-dish type of evaporation of the Freon-TF/Sunisc fluid. Evaporation tests of this kind are not incorporated into ASTM or other standard test procedures. However, the test is a common one offered by several commercial testing laboratories. Usually such tests have a duration of 24 to 48 hours. In addition to shallow open-dish evaporation, volatilization losses were measured from an open vessel filled so that the exposed surface was exactly 1/6 of the total liquid surface (one side of an open cube). It can be shown that this condition is met in a cylindrical container when the depth of the liquid is equal to the diameter of the vessel. In both tests loss of Freon-TF from the fluid was measured by weighing the specimens at regular intervals during the test period.

In the shallow open-dish experiment a 35 gram specimen (approximately 25 ml volume) was placed in a dish 56 mm in diameter, giving a fluid depth of 10 mm. The dish was placed on the pan of a torsion balance in a location having minimal air movement. As shown by the weight loss measurements presented in Table 60 and plotted in Figure 49, most of the Freon-TF was lost in approximately 50 minutes.

In the second evaporation experiment, the exposed surface of the fluid was much smaller, relative to the total volume of fluid, than in the previous experiment. A short cylindrical weighing jar was filled so that one-sixth of the total fluid interface was exposed to the air, as discussed above. The vessel was placed on the pan of a balance which was maintained in a static air atmosphere. The evaporation rate was monitored at five minute intervals for the first half-hour and, thereafter, at longer intervals for 31 hours. Two separate phases unexpectedly appeared in the fluid quite early in this test. Observation of the evaporation process showed that some of the Freon-TF vapors tended

TABLE 60. EVAPORATION LOSS OF FREON-TF/SUNISO FLUID FROM SHALLOW OPEN DISH

Elapsed time, minutes	Weight loss of 34.3 gram sample, g	Weight loss, %
2.5	4.1	11.9
4	5.8	16.9
6	7.8	22.7
8.5	9.8	28.6
12	12.8	37.3
16.5	15.8	46.1
19.5	17.8	51.9
23.5	19.8	57.7
35.5	25.8	75.2
49.5	27.3	79.6

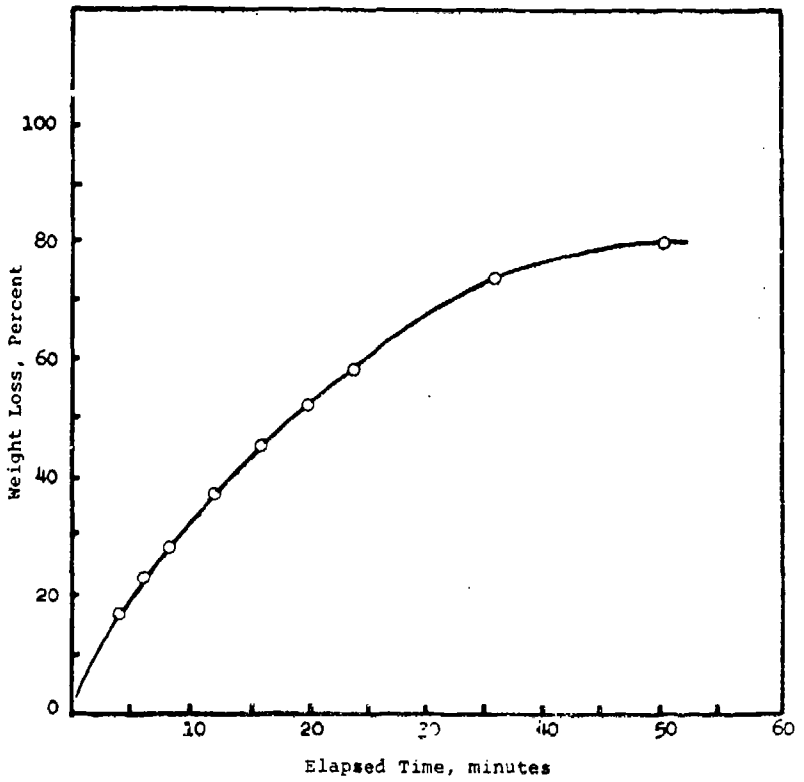


Figure 49. Evaporation of Freon-TF/Suniso 3GS from open dish in static air.

to recondense on the lip or small inner surface of the weighing jar. Due to it having a much greater specific gravity than the fluid, the pure Freon traveled down the inner surface of the vessel and accumulated in a layer at the bottom. The sharp interface of the two layers was quite evident within 30 minutes. As the Freon was isolated at the bottom of the vessel, its rate of evaporation decreased markedly as shown in Figure 50, Curve B and Table 61.

This phenomenon prompted a third evaporation experiment identical to the second except that the fluid was mixed at the time of each weighing to insure homogeneity. Under these circumstances, most of the Freon-TF was lost from the fluid in 8 to 10 hours. Data for these tests are presented in Table 62 and shown in Figure 50, Curve A.

Lubricity Measurements

A number of mechanical devices are in current use for the evaluation of lubricity, the Falex machine, the Four-Ball tester and the Ball-on-cylinder tester, to name a few. Each test differs slightly in the information it supplies, and there is presently no single one which represents a standard measure for lubricating properties. A test frequently used for fluids at Monsanto Industrial Chemicals Company (MIC) is the Four-Ball tester. In this test, a steel ball is rotated under a load against three stationary balls which are immersed in the fluid. The diameter of the wear scars on the stationary balls are measured after completion of the test. The Four-Ball tester was employed for this investigation on the following fluids:

- Calibrating Fluid, Mil-F-7024B (containing one ounce Hitec E515 per 400 gallons of fluid)
- Freon-TF/Suniso 3GS oil (81.8%, 18.2% by weight)
- Exxon FN 3146

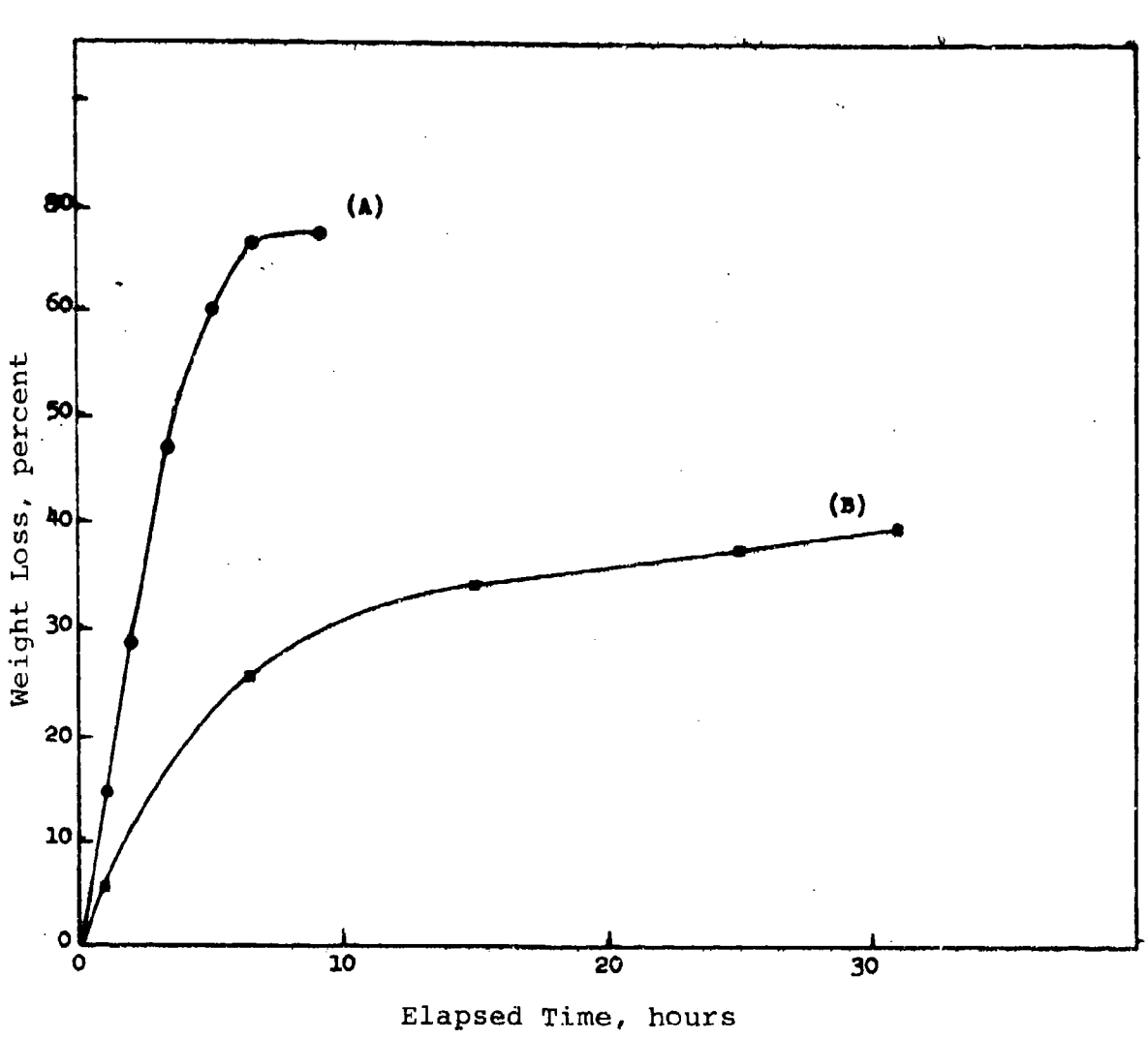


Figure 50. Evaporation of Freon-TF/Suniso 3GS fluid from weighing jar with diameter equal to fluid depth: (a) periodic agitation, (b) no agitation.

TABLE 61. EVAPORATION LOSS OF FREON-TF SUNISO FLUID FROM SHORT CYLINDRICAL WEIGHING JAR WITHOUT AGITATION*

Elapsed time, minutes	Weight loss of 84-gram sample, g	Percent weight loss, %
5	0.6	0.7
10	1.1	1.3
15	1.6	1.9
20	2.1	2.5
25	2.6	3.1
30	3.1	3.7
hours	(86-gram sample)†	
1	5.2	6.0
2	9.5	11.0
6.5	21.7	25.1
15	29.2	34.0
25	32.1	37.2
31	34.0	39.4

*Stratification of components occurred due to refluxing action of Freon-TF.

†Experiment continued with fresh sample.

TABLE 62. EVAPORATION LOSS OF FREON-TF SUNISO FLUID FROM SHORT CYLINDRICAL WEIGHING JAR WITH FREQUENT AGITATION*

Elapsed time, hours	Weight loss of 86-gram sample, g	Percent weight loss, %
1	14.5	16.9
2	28.7	33.5
3.5	46.9	54.7
4.75	59.9	69.9
6.5	66.2	77.2
9.25	66.7	77.8

*Agitation prevented stratification of components.

The duration of the test for each fluid was one hour and the rate of rotation was 1850 rpm. A 10-kilogram load was placed on the rotating ball. Most lubricity test devices including the Four-Ball tester, are not ordinarily used for highly volatile samples. Even though the tests were conducted at 72°F, the Freon/Suniso fluid had to be replenished during the test due to evaporation losses. Similarly, one half of the Freon-TF/FN 3146 blend was lost by evaporation during the test. This loss corresponds to about the volume of Freon-TF in the fluid. Consequently, during the latter part of the test, nearly pure Exxon FN 3146 oil was in the tester reservoir.

For the first fifteen minutes of the test on the Freon-TF/Suniso blend, the tester was very noisy, indicating a fluid with poor lubricating properties. As the test progressed and the oil concentration increased due to Freon evaporation, the noise decreased. Test results are presented in Table 63. Despite the shortcomings mentioned above, the test results appear to be useful in suggesting that the Freon-TF/Suniso 3GS blend has lower lubricity than fluid Mil-F-7024 and that the Freon/FN 3146 blend probably has lubricity at least equal to the reference fluid. It should be noted that the corrosion inhibitor, Hitec E515, is known to increase fuel lubricity. This additive was present in fluid Mil-F-7024 but not in the other fluids.

Discussion

The data generated in this investigation require little explanation. The Freon-TF/Suniso 3GS blend shows excellent compatibility with the test elastomers, even in the 45-day contact period. The lubricity of this fluid appears to be not quite as good as Mil-F-7024 fluid, however, this might be improved considerably by the appropriate additive. Composition changes due to evaporation of Freon-TF will be a problem unless the fluid is used in a closed system. Evaporation experiments have shown that no constant-boiling composition of the two fluid components exists.

TABLE 53. COMPARISON OF LUBRICATING PROPERTIES OF FLUIDS AND FLUID BLENDS USING FOUR BALL TESTER*

Fluid	Scar diameter, mm	Comments
1. Mil-F-7024B†	1.05	Uniform wear, brown stain around scar.
2. Freon-TF/Suniso 3GS	1.52	Uniform wear, slight to medium sludge deposit, very noisy for the first 15 min of test. Fluid replenished during test.
3. Freon-TF/Exxon FN3146	0.72	Uniform wear, dark brown stain around scar. One half of fluid evaporated during test.
4. Exxon FN3146	0.80	Uniform wear, brown stain and deposit.

*10 Kg load, 1850 RPM for 1 hour.

†Contains corrosion inhibitor, Hitec 515.

Freons 11 and 12 are currently being scrutinized because of their potential effect on the Earth's protective ozone layer. These materials diffuse into the stratosphere where they are decomposed by U.V. radiation from the sun. This causes the release of fluorocarbon radicals and free chlorine atoms which decrease the average concentration of ozone through catalytic chain reactions. To date, Freon-TF has not been mentioned in connection with this problem, however, due to its chemical similarity with compounds currently being investigated, it too may become embroiled in controversy. A factor which should be considered in evaluating the Freon-TF/Suniso 3GS fluid is the possibility that it might eventually be subject to environmental regulations.

7. DETERMINATION OF BENZENE IN JP-4

Recent health restrictions which have been placed on human exposure to benzene vapors have created the need for a rapid accurate means for analysis of benzene in hydrocarbon fuels. CEC Model 21-103C mass spectrometer having a batch sample inlet was shown to provide an excellent means of conducting the analysis.

Samples consisting of a JP-4 fuel, and that fuel spiked with benzene, were analyzed to determine benzene content.

JP-4 fuel	0.29% benzene by weight
JP-4/benzene	1.26% benzene by weight

A chromatographic separation of benzene from other fuel components was also conducted using a 50-meter glass capillary column coated with SF- 96 stationary phase. Cyclohexane and benzene were identified by their retention times and are labeled on the partial chromatograms shown in Figures 51 and 52. After elution of benzene, the column temperature was rapidly increased to rid it of remaining fuel. Both mass spectrometry and high resolution gas chromatography provide a rapid and sensitive means of determining benzene content in fuels.

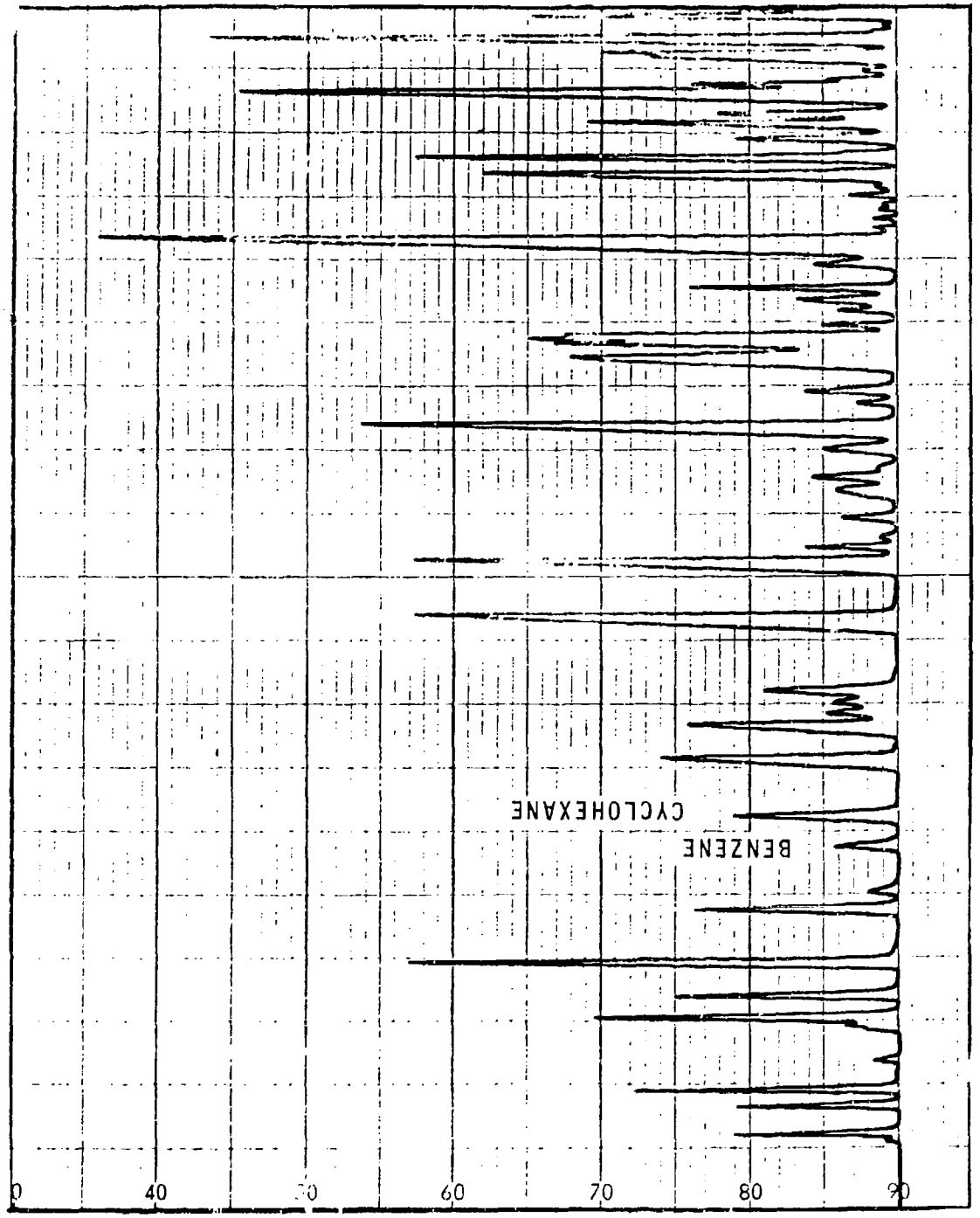


Figure 51. Portion of JP-4 chromatogram showing resolution of benzene from surrounding components

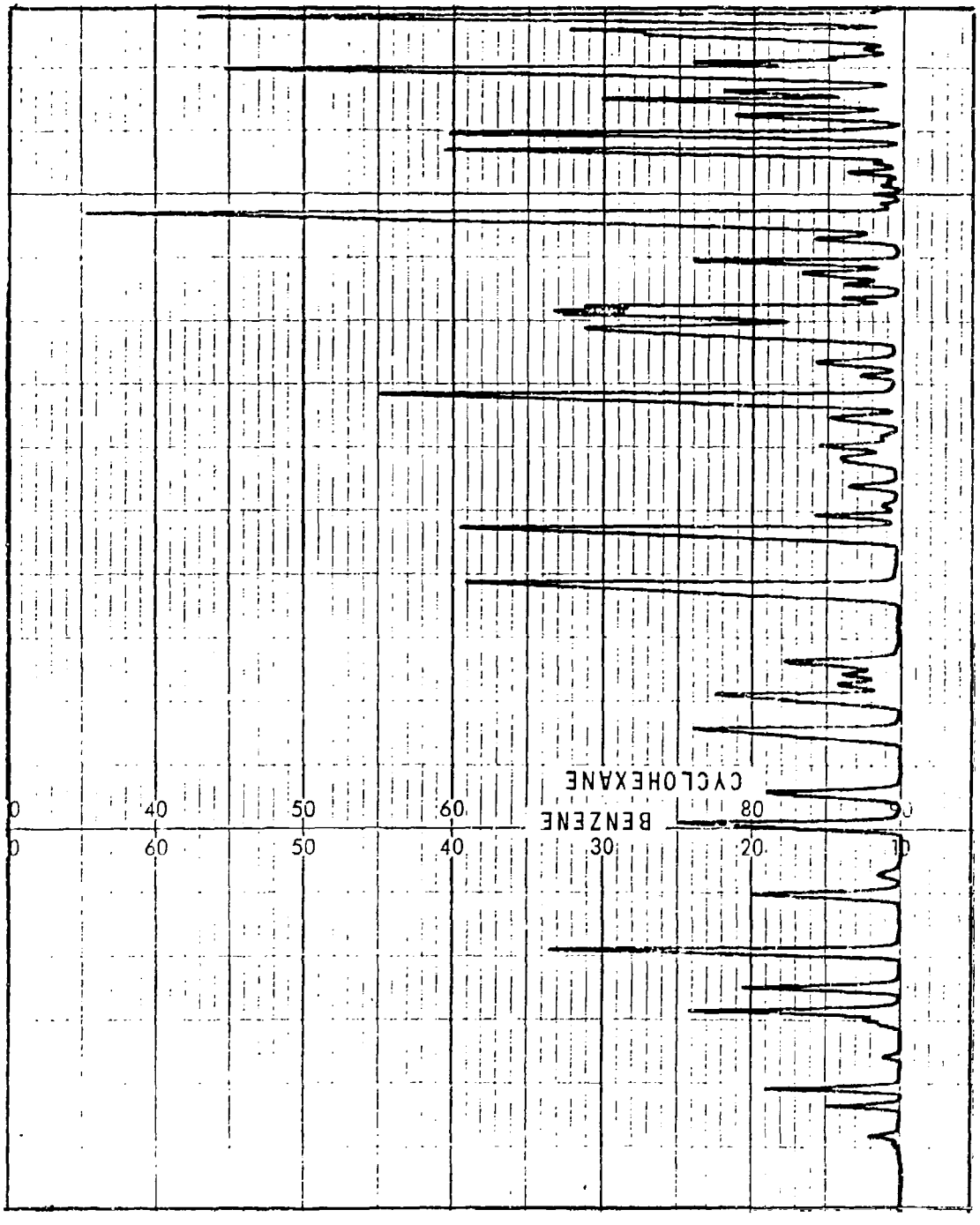


Figure 52. Portion of chromatogram of JP-4 fuel spiked with benzene

SECTION IV

COMBUSTION SUPPORT STUDIES

A large number of fuel specimens have been physically and chemically characterized as a part of an Air Force contractual combustion program to study the consequences of modifying conventional JP-4 and JP-8 fuels. Baseline fuels were characterized, as well as those fuels after increasing their aromatic content or boiling range by use of suitable blending stocks.

1. ANALYSIS OF JP-8 FUEL AND AROMATIC BLENDING STOCKS

Elemental and hydrocarbon type analyses were conducted on a baseline JP-8 fuel and two aromatic blending stocks. These materials were used by the Air Force for preparing special fuel blends for combustion testing.

Hydrocarbon Type Analysis

Hydrocarbon type analyses were conducted on the three specimens by mass spectrometry. Generally the accuracy of a hydrocarbon type analysis by this means depends upon the degree to which the sample fits the boiling range requirements of the method. Since the boiling range of the aromatic blending stocks were unspecified, the samples were analyzed by gas chromatography, as shown in Figures 53 through 55, prior to selecting the hydrocarbon type analysis method. All components of the xylene composite were found to fall within the gasoline range, thus a procedure similar to ASTM D2789 was selected for the analysis. The 2040 solvent was found to have approximately the same boiling range as the JP-8 so these samples were analyzed by ASTM D2425. Both procedures involved the summation of mass spectral line intensities which are characteristic of the amounts of different hydrocarbon species. For the JP-8 specimen, a preliminary column chromatographic

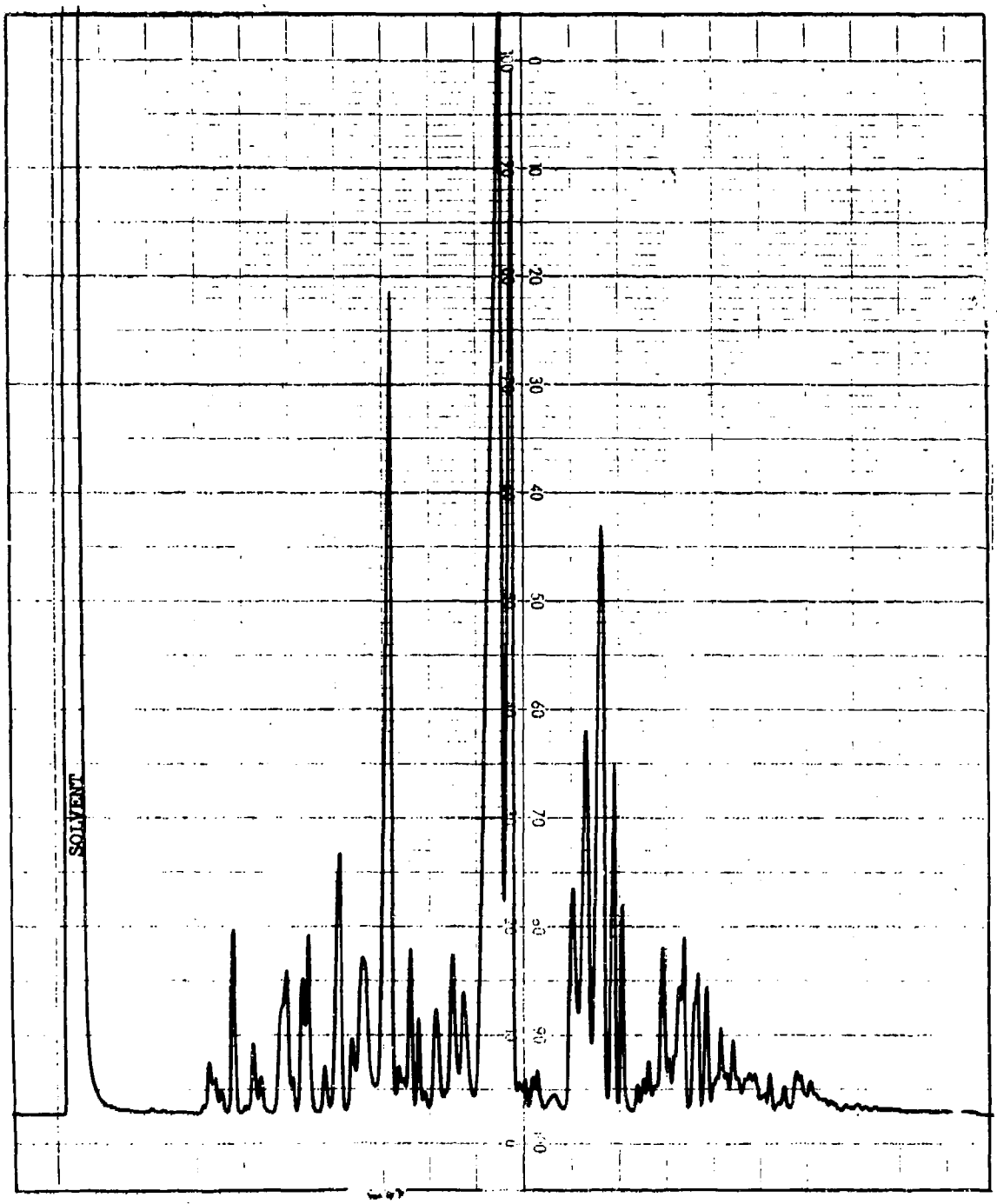


Figure 53. Gas chromatogram of 2040 solvent.

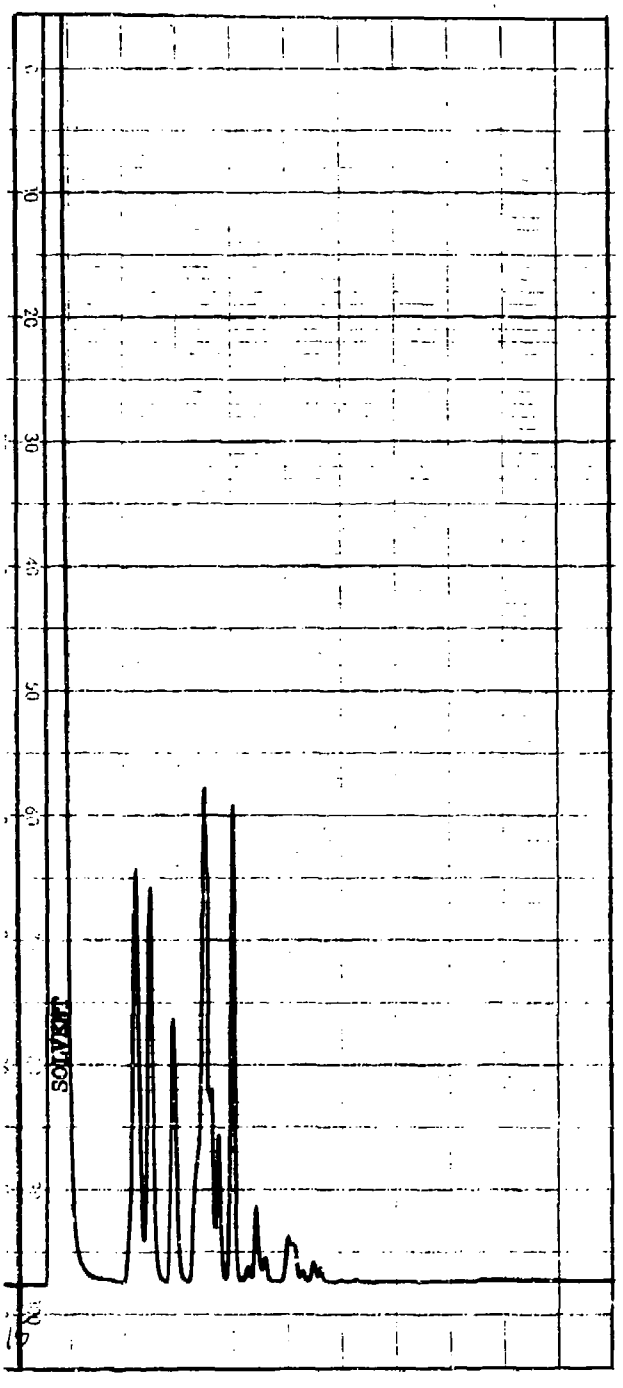


Figure 54. Gas chromatogram of xylene composite.

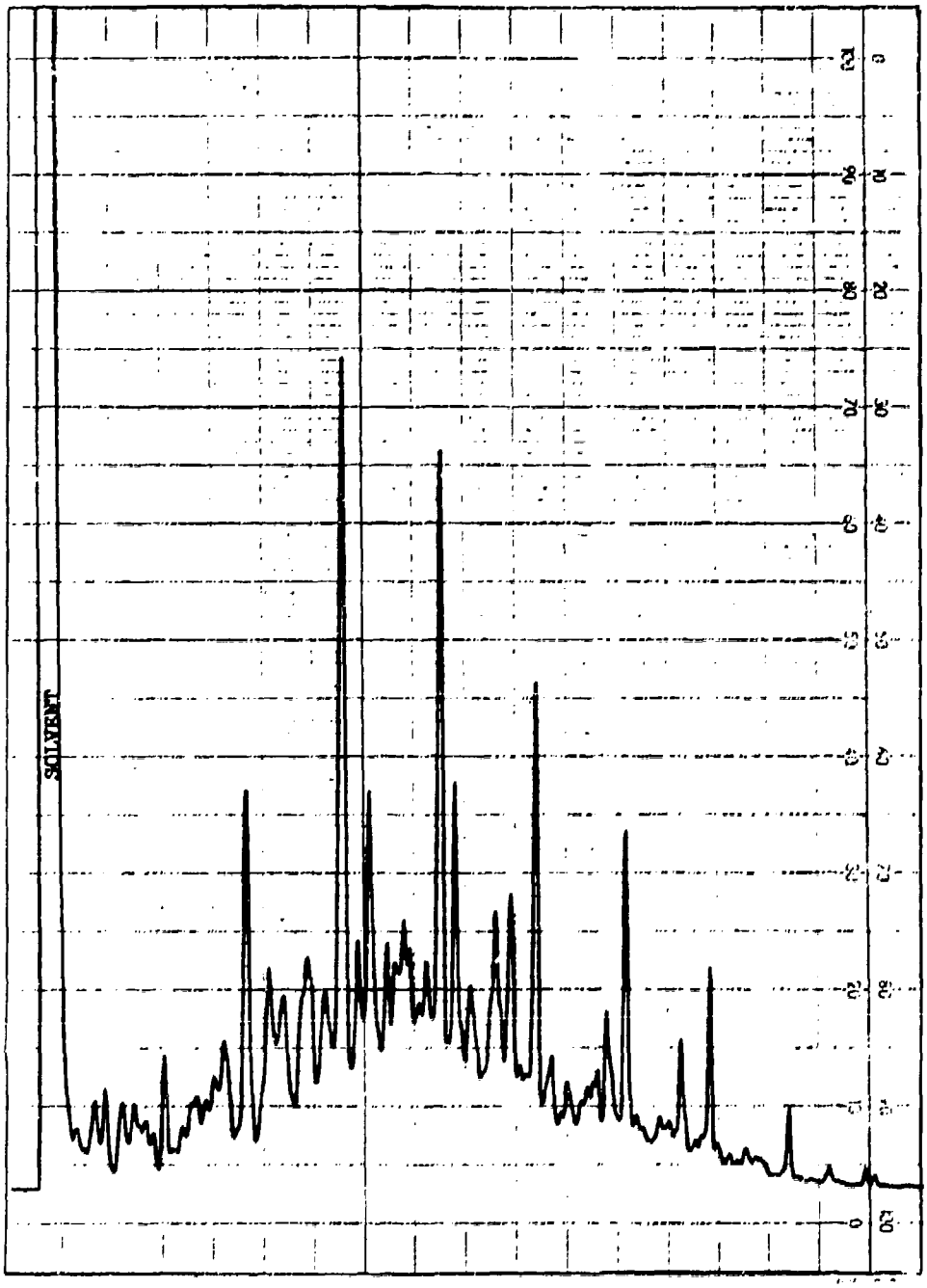


Figure 55. Gas chromatogram of JP-8 fuel.

separation into saturate and aromatic fractions was required. The separation was conducted over a column of activated bauxite and silica gel (ASTM 2549). The results of these analyses are presented in Table 64.

Elemental Analyses

In order to firmly establish the composition of the three materials and determine the reliability of interlaboratory analyses, each specimen was submitted to three independent micro-analytical laboratories of excellent repute for carbon and hydrogen analysis. Laboratories selected for this work were:

Laboratory A	Sanda, Inc. Philadelphia, Pa.
Laboratory B	Galbraith Laboratories, Inc. Knoxville, Tenn.
Laboratory C	Schwarzkopf Laboratory, Inc. Woodside, N.Y.

Results of the analyses are reported in Table 65. Grand mean values, equally weighting all analyses, have been calculated for each sample. By comparing results from each laboratory with the grand mean, Lab A is shown to have the smallest deviation for the 2040 solvent, Lab B the smallest deviation for the JP-8 and Lab C the smallest deviation for the xylene composite. Thus it is difficult to establish that one laboratory has a better analysis than the others. The average of the deviation from the grand mean for the three analyses by each laboratory has been calculated and might be used as a factor in assessing reliability. These values are:

	Carbon	Hydrogen
Lab A	0.10	0.08
Lab B	0.18	0.11
Lab C	0.17	0.11

TABLE 64. HYDROCARBON-TYPE ANALYSIS

	JP-8		Xylene Composite		2040 Solvent	
	Weight, %	Average Carbon No.	Weight, %	Average Carbon No.	Weight, %	Average Carbon No.
Paraffins	41.8	12.1	-	-	-	-
Cycloparaffins	37.5	12.0	-	-	-	-
Dicycloparaffins	6.1		-	-	-	-
Tricycloparaffins	1.1		-	-	-	-
Alkylbenzenes	7.5	10.9	100.0	8.9	35.5	10.5
Indans/Tetralins	3.8		-	-	6.8	11.0
Indenes	0.7		-	-	0.09	11.0
Naphthalene[a]	-[b]		-	-	18.6	10.0
Naphthalenes	1.5	11.6	-	-	39.0	11.2
Acenaphthenes	-		-	-	-	-
Acenaphthylenes	-		-	-	-	-
Tricyclic aromatics	-		-	-	-	-
Analytical Method	ASTM D2549 and ASTM D2425		ASTM D2789		ASTM D2425	

(a) Refers to the unsubstituted compound.

(b) Dash indicates none was detected.

TABLE 65. ELEMENTAL ANALYSIS OF HYDROCARBON SAMPLES
WEIGHT PERCENT CARBON AND HYDROGEN

	JP-8		Xylene Composite		2040 Solvent	
	C	H	C	H	C	H
Lab A	85.90	14.003	90.16	9.82	91.59	8.41
	85.98	14.005	90.20	9.80	91.57*	8.42*
Mean	85.94	14.004	90.18	9.81	91.61	8.38
Deviation from Grand Mean	0.09	0.11	0.14	0.04	0.07	0.08
Lab B	85.96	13.93	89.95	9.78	91.96	8.11
	85.73	14.04	89.80	9.94	92.04	8.06
Mean	85.84	13.99	89.83	9.86	92.00	8.08
Deviation from Grand Mean	0.01	0.10	0.21	0.01	0.32	0.22
Lab C	85.87	13.77	90.02	9.85	91.35	8.46
	85.67	13.59	90.22	9.93	91.57	8.33
Mean	85.77	13.68	90.12	9.89	91.46	8.39
Deviation from Grand Mean	0.08	0.21	0.08	0.04	0.22	0.09
Grand Mean	85.85	13.89	90.04	9.85	91.68	8.30
Average Deviation	0.06	0.14	0.14	0.03	0.20	0.13

*Analyst conducted a third analysis on this sample because of the unexpectedly high carbon content.

Values for Labs B and C are nearly identical but are somewhat smaller for Lab A, indicating that, overall, determinations by Lab A fell closer to the mean. This is, of course, not a measure of accuracy but of reproducibility. It should be noted that, generally, the analyses by all laboratories are typical of results that might be expected for samples of this type.

As a measure of the extent to which the hydrocarbon-type analysis data from Table 66 can be reconciled with the elemental analyses, the former data were used to calculate a theoretical percent carbon for each sample. The contribution to the carbon content of each hydrocarbon class is detailed in Table 66. The resulting values are presented in that table and are shown to compare well with results of elemental analyses.

2. CHARACTERIZATION OF JP-8 AND MODIFIED JP-8 FUELS

Three fuels were subjected to eight separate analytical procedures to provide their full physical and chemical characterization. The samples consisted of a baseline JP-8 and two JP-8 specimens which had been modified by the addition of 2040-solvent to increase aromatic content and Gulf Mineral Oil to increase the final boiling point. A fourth fuel of undesignated origin was included in some of the tests to determine whether its composition matched that of any other of the three fuels.

The subject fuels were intended for use in Air Force sponsored combustion test programs.

Simulated Distillation by Gas Chromatography

Simulated distillations were conducted according to ASTM Method D2887 to determine boiling point distributions. A Hewlett-Packard Model 5710 A gas chromatograph, having a hydrogen flame ionization detector, was employed. Data were recorded and

TABLE 66. RECONCILIATION OF ELEMENTAL AND HYDROCARBON TYPE ANALYSES

	JP-8		Xylene Composite		2040 Solvent	
	Average compound	Contribution to carbon content, Wt %	Average compound	Contribution to carbon content Wt %	Average compound	Contribution to carbon content, Wt %
Paraffins	$C_{12.1}H_{26.2}$	35.83	-	-	-	
Cycloparaffins	$C_{12}H_{24}$	31.76	-	-	-	
Dicycloparaffins	$C_{12}H_{22}$	5.29	-	-	-	
Tricycloparaffins	$C_{12}H_{20}$	0.96	-	-	-	
Alkylbenzenes	$C_{10.9}H_{15.8}$	6.69	$C_{8.9}H_{11.8}$	90.05	$C_{10.5}H_{15}$	31.70
Indanes/Tetralins	$C_{11}H_{14}$	3.43	-	-	$C_{11}H_{14}$	6.15
Indenes	$C_{11}H_{12}$	0.64	-	-	$C_{11}H_{12}$	0.08
Naphthalene		-	-	-	$C_{10}H_8$	17.50
Naphthalenes	$C_{11.6}H_{11.2}$	1.38	-	-	$C_{11.2}H_{10.4}$	36.25
Calculated total carbon		85.99		90.05		91.42
Total carbon by elemental analysis		85.85		90.04		91.68

computed by an HP-3350 laboratory data system. The chromatographic column was a 6 ft x 1/8 in. stainless steel tubing containing 3% OV-1 on 100/120 mesh Chromosorb W, AW DMSC. Helium was the carrier and air was used as the oxidant. The column temperature was programmed from 50°C to 270°C at 8°C per minute. Boiling point distribution data are presented in Table 67. Method ASTM D2887 specifies low resolution chromatographic conditions, with required resolution being between 3 and 8. Resolution for this purpose is defined as the separation, in mm, between C_{16} and C_{18} peaks, divided by one-half the sum of the baseline width of the peaks, also in mm. In addition to the low resolution chromatograms from which the data in Table 67 were taken, higher resolution chromatograms were recorded (Figures 56-59) to facilitate comparison of samples. A chromatogram of 2040 solvent appeared in the previous subsection. Examination of chromatograms indicates that the unidentified fourth fuel sample, Figure 60, is identical to the JP-8/Gulf MSO blend, Figure 61.

Density was determined in the temperature range of 0 to 100°F using the dilatometer method. Kinematic viscosity was measured according to ASTM Method D445. Data are presented in Table 68 and 69. Heat of combustion was determined by the oxygen bomb calorimeter according to ASTM D240. Gross and net heat of combustion values are presented in Table 70. Surface tension as a function of temperature was determined by the capillary-rise method. No contact angle correction was required for these measurements. Data and equations for computing values at various temperatures are presented in Table 71. Vapor pressure measurements as described in Appendix B were conducted on the specimens. Values and equations are presented in Table 72. Plots of log vapor pressure versus $\frac{1000}{T°K}$ are presented in Figure 60.

TABLE 67. BOILING POINT DISTRIBUTION

Percent recovered	JP-8 °F	JP-8 °C	JP-8/2040 Solvent °F	JP-8/2040 Solvent °C	JP-8/Gulf MSO °F	JP-8/Gulf MSO °C
0.5 (initial boiling point)	248	120	248	120	248	120
5	311	155	316	158	313	156
10	345	174	340	171	335	168
20	370	188	370	188	365	185
30	394	201	390	199	392	200
40	405	207	414	212	423	217
50	428	220	437	225	450	232
60	450	232	457	236	478	248
70	475	246	484	251	509	265
80	500	260	505	263	543	284
90	531	277	536	280	577	303
99.5 (Final boiling point)	592	311	597	314	653	345

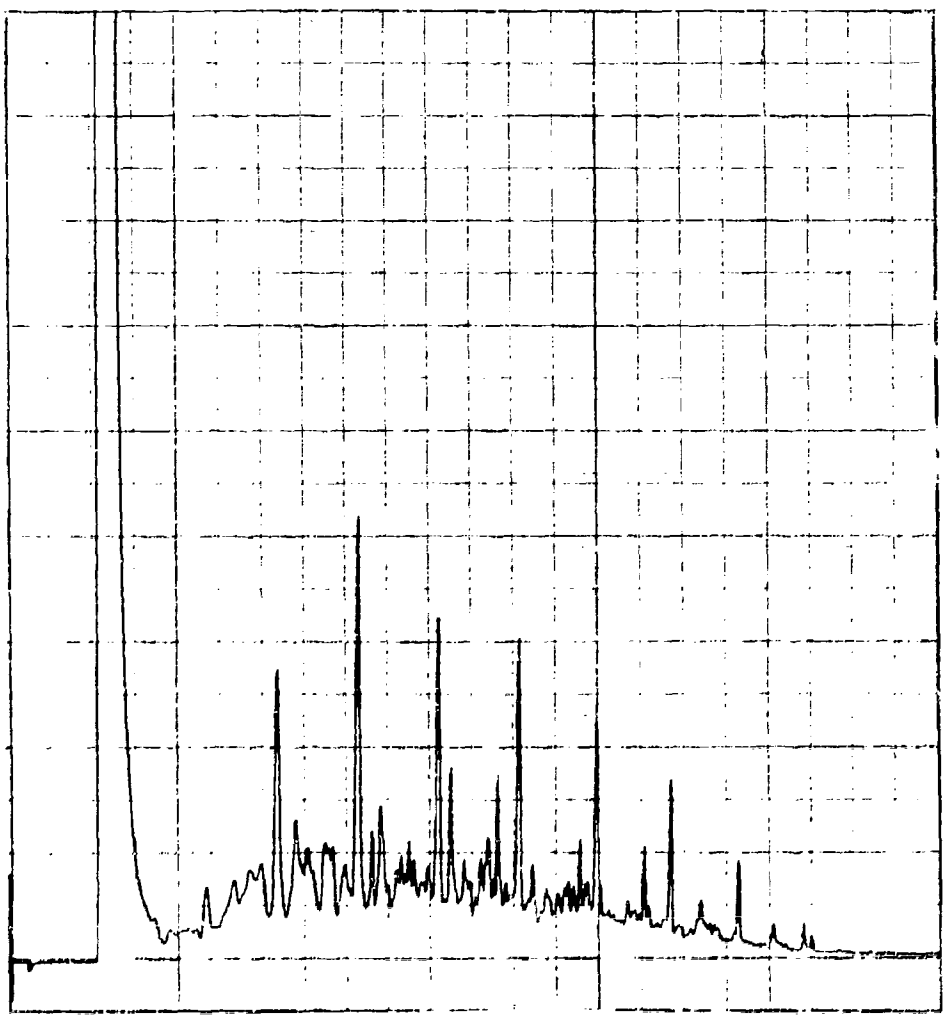


Figure 56. Chromatogram of M-8, 7 July 197".

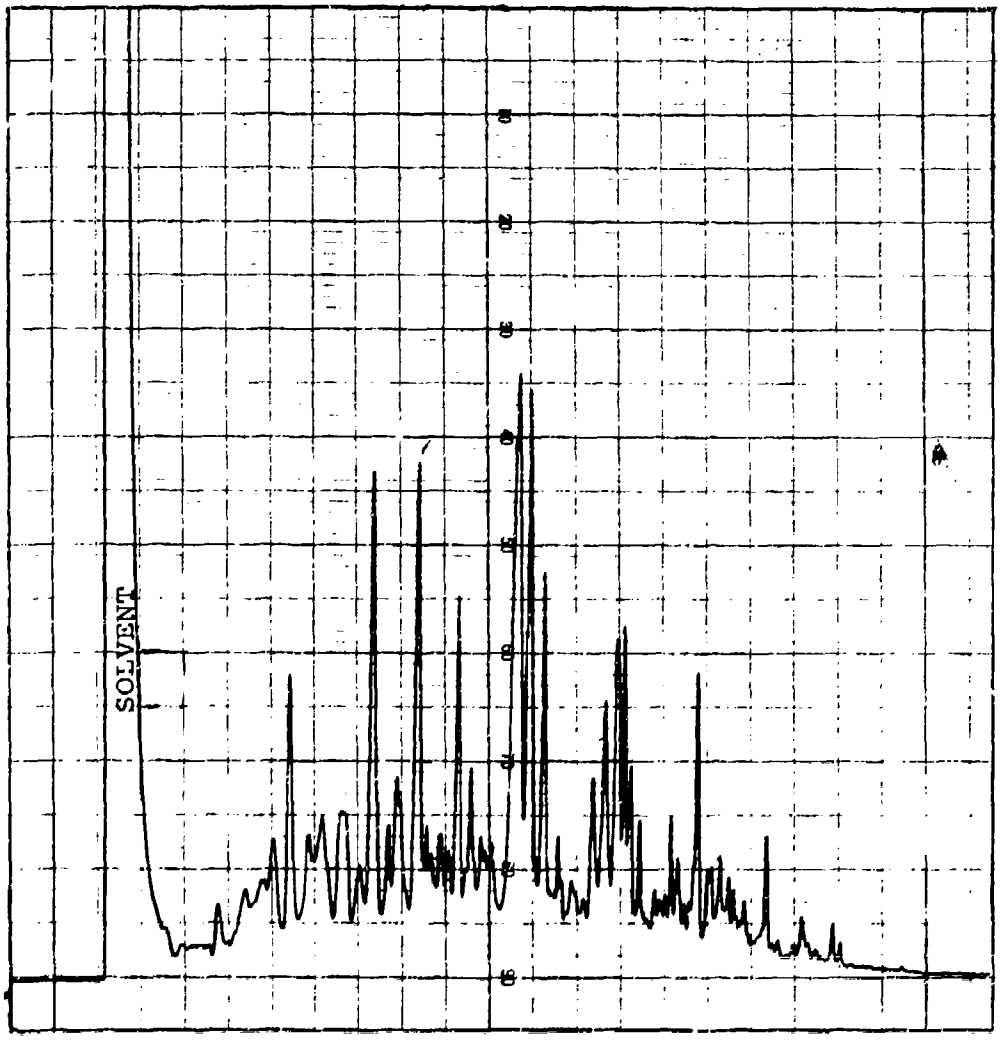


Figure 57. Chromatogram of JP-8 with 2040 solvent.

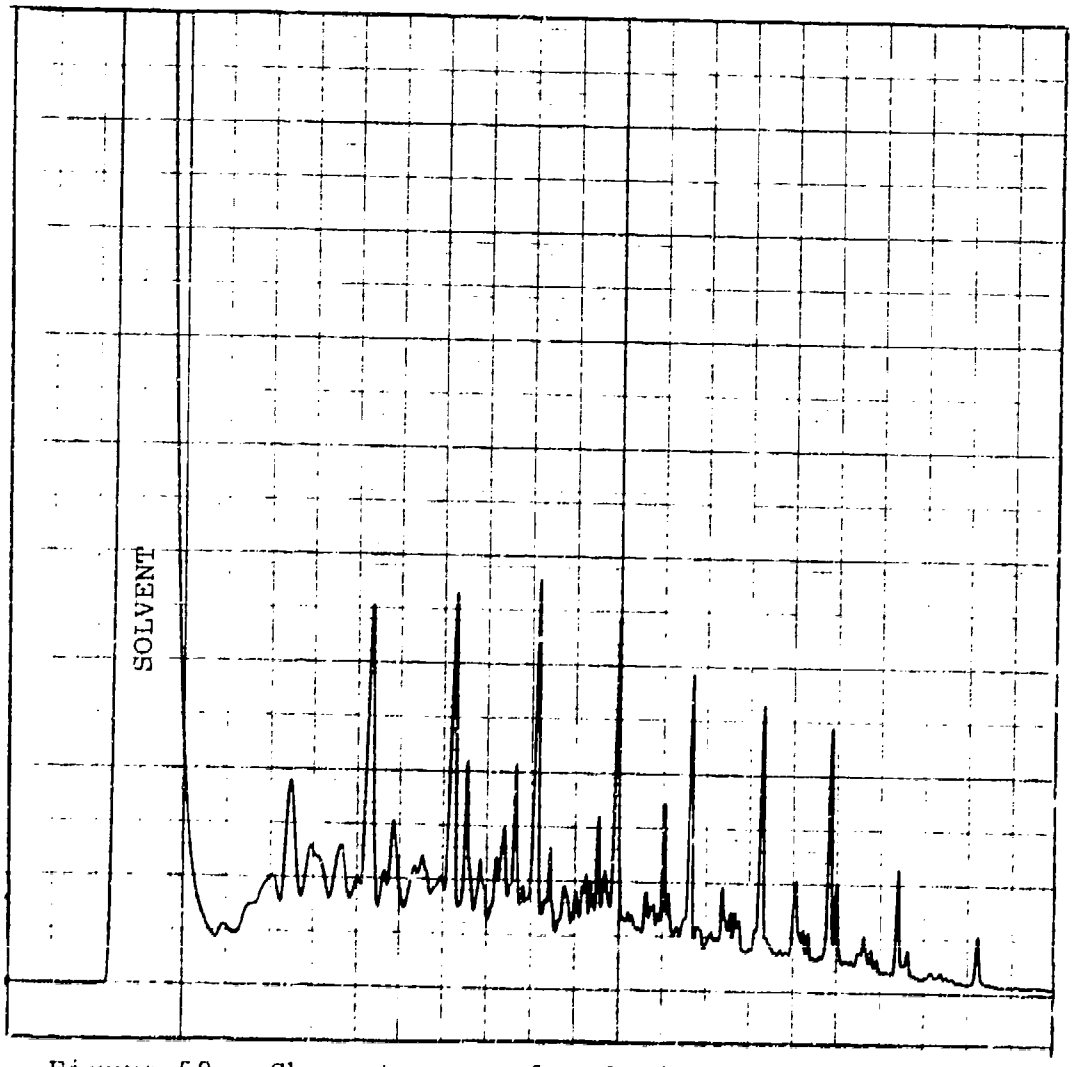


Figure 58. Chromatogram of undesignated fuel sample.

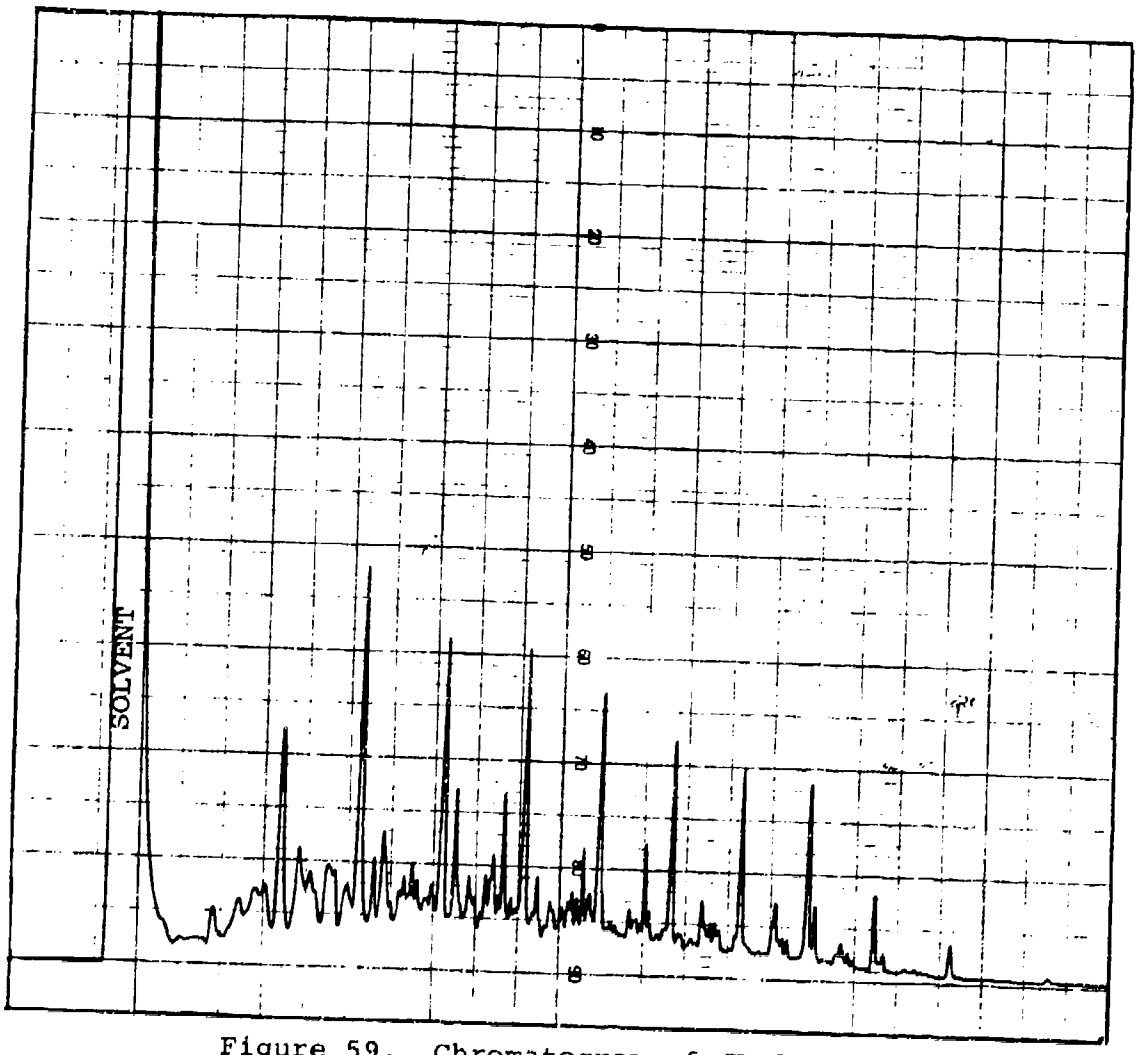


Figure 59. Chromatogram of JP-8 with Gulf Mineral Seal Oil.

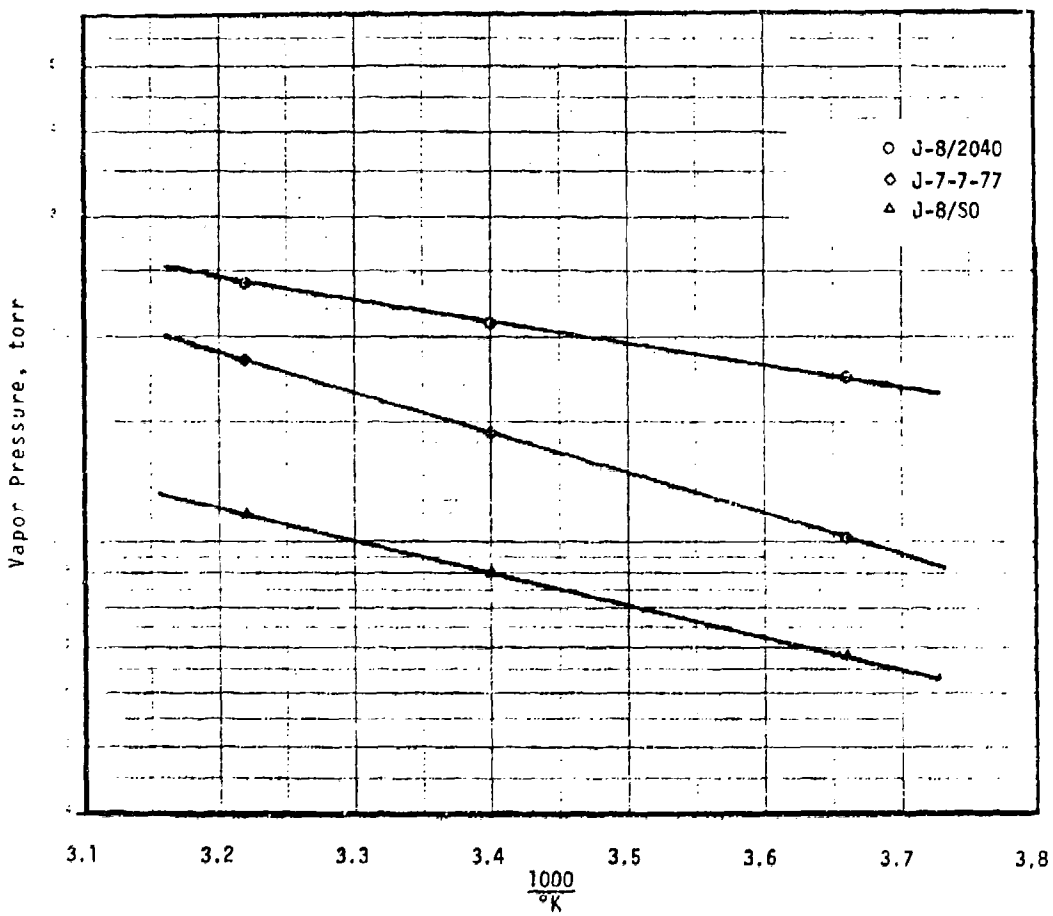


Figure 60. Vapor pressure plot for JP-8 test fuels.

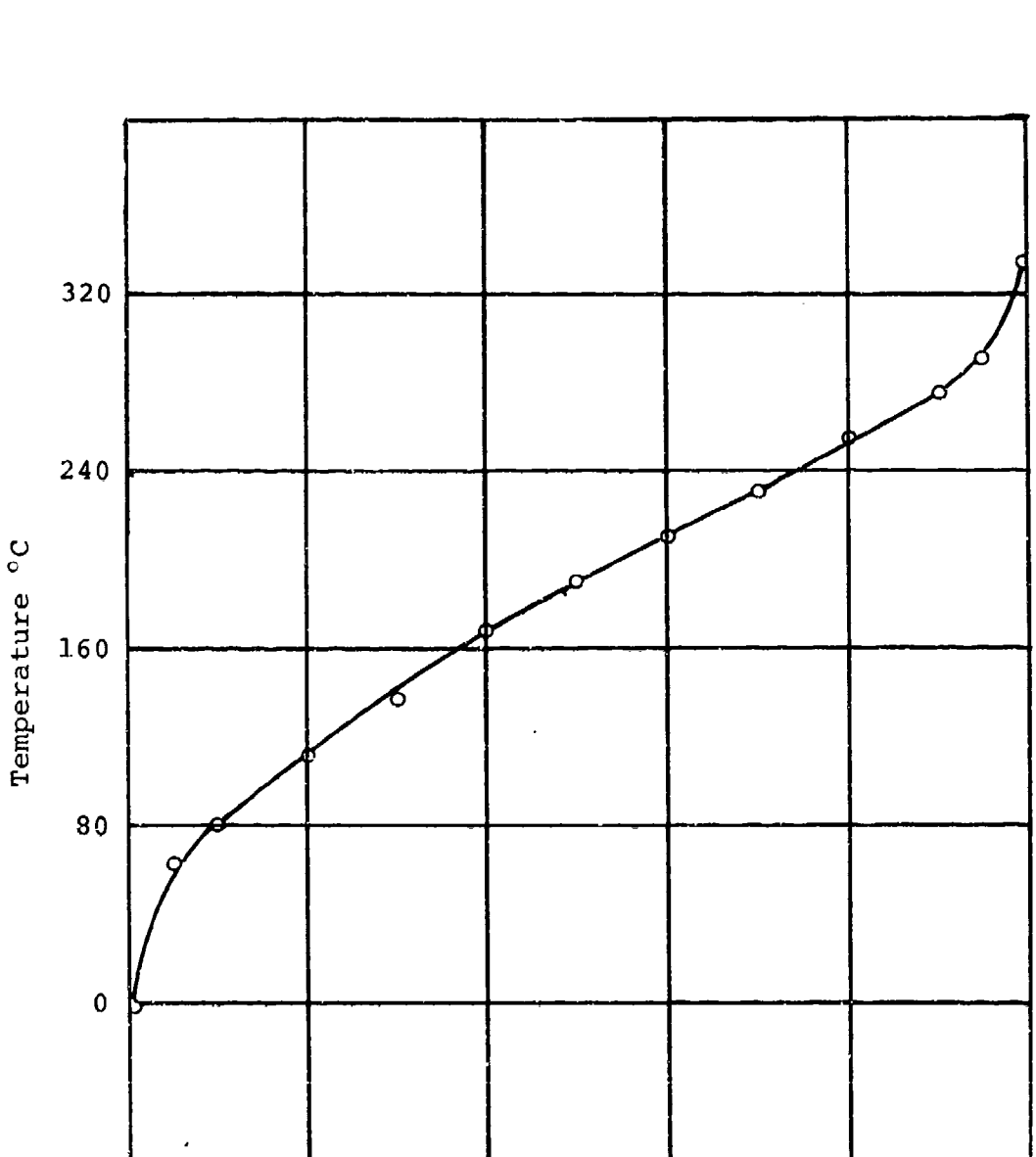


Figure 61. Boiling point distribution plot of JP-8/2040 blend.

TABLE 68. DENSITY OF TEST FUELS

Sample	Grams/cc		
	0°F(-18°C)	77°F(25°C)	100°F(38°C)
JP-8, 7 July 1977	0.8329	0.8008	0.7913
JP-8 w/2040 solvent	0.8765	0.8437	0.8342
JP-8 w/Gulf MSO	0.8345	0.8025	0.7932
Undesignated fuel	0.8339	0.8027	0.7931

TABLE 69. KINEMATIC VISCOSITIES OF TEST FUELS

Fuel	Centistokes		
	0°F	77°F	100°F
JP-8, 7 July 1977	5.288	1.897	1.533
JP-8 w/240 solvent	5.316	1.856	1.498
JP-8 w/Gulf MSO	6.343	2.135	1.708
Undesignated fuel	6.336	2.128	1.711

TABLE 70. HEAT OF COMBUSTION

Sample	Gross		Net	
	Btu/lb	Cal/g	Btu/lb	Cal/g
JP-8/2040	19,178	10,654	18,067	10,037
JP-8/7-7-77	19,768	10,982	18,494	10,274
JP-8/SO	19,782	10,990	18,503	10,279

TABLE 71. SURFACE TENSION OF TEST FUELS AS A FUNCTION OF TEMPERATURE

Sample	Dynes cm^{-1} 32°F	70°F	100°F	Equation
JP-8, 7 July 1977	27.98	26.14	24.76	$\gamma = -0.0474(T°F) + 29.48$
JP-8, w/2040 solvent	28.91	27.32	26.26	$\gamma = -0.0391(T°F) + 30.13$
JP-8, w/Gulf MSO	27.99	26.14	24.36	$\gamma = -0.0461(T°F) + 29.44$
Undesignated fuel	28.18	26.42	25.36	$\gamma = -0.0417(T°F) + 29.46$

TABLE 72. VAPOR PRESSURE OF TEST FUELS AS A FUNCTION OF TEMPERATURE

	Pressure, torr 32°F(0°C)	70°F(21°C)	100°F(38°C)	Equation
JP-8, 7 July 77	10	14.5	18.5	$\log P = -0.5980\left(\frac{1000}{T°K}\right) + 3.1934$
JP-8 w/2040 solvent	17.5	21	24	$\log P = -0.3113\left(\frac{1000}{T°K}\right) + 2.3819$
JP-8 w/Gulf MSO	7	9	11	$\log P = -0.4743\left(\frac{1000}{T°K}\right) + 2.5680$

Elemental Analysis

The fuel specimens were submitted to three independent micro-analytical laboratories for carbon and hydrogen analyses. The laboratories were:

Lab A Sanda, Inc., Philadelphia, Pa.
Lab B Galbraith Laboratories, Knoxville, Tenn.
Lab C Schwarzkopf Laboratory, Woodside, N.Y.

Analyses are presented in Table 73.

Hydrocarbon-type analyses were conducted on the three fuels. The fuels were separated into aromatic and paraffinic fractions by column chromatography (ASTM 2549) prior to conducting the analysis. A CEC-21-103 mass spectrometer was used as described in ASTM 2425. Analyses are presented in Table 74.

3. CHARACTERIZATION OF TWO JP-4 FUELS

Two samples of JP-4 fuel, labelled Tank B-11 and 8-24-77 were subjected to a number of physical property measurements. Density, kinematic viscosity, vapor pressure and surface tension as a function of temperature, and net heat of combustion were measured. These data are presented in Tables 75 and 76.

A simulated distillation by gas chromatography was conducted (ASTM D2887) and data are given in Table 77.

Heat of combustion was determined using the oxygen bomb calorimeter as described in ASTM D240. Data are presented in Table 78. Hydrocarbon type analyses were conducted by mass spectrometer and are presented in Table 79.

TABLE 73. ELEMENTAL ANALYSIS OF TEST FUELS

	Lab A		Lab B		Lab C		Grand Mean	
	%C	%H	%C	%H	%C	%H	%C	%H
JP-8, 7 June 77	86.06	13.94	85.96	13.93	86.07	14.25		
	86.00	14.00	85.86	14.09	86.05	14.19		
Average	86.03	13.97	85.91	14.01	86.06	14.22	86.00	14.07
JP-8 w/2040 solvent	87.82	12.18	87.80	12.16	87.38	12.66		
	87.81	12.18	87.66	12.23	87.66	12.60		
Average	87.81	12.18	87.73	12.19	87.52	12.63	87.69	12.33
JP-8 w/Gulf Seal Oil	85.95	14.05	85.16	13.90	85.95	14.16		
	85.99	14.00	85.25	13.76	86.03	14.17		
Average	85.97	14.02	85.22	13.83	85.99	14.16	85.73	14.00
Undesignated fuel	86.00	14.00	86.59	13.57	85.97	13.89		
	85.98	14.02	86.48	13.60	86.01	13.92		
Average	85.99	14.01	85.53	13.58	85.99	13.90	85.84	13.83

TABLE 74. HYDROCARBON TYPE DISTRIBUTION IN BASELINE AND MODIFIED JP-8 FUELS

Compound Type	Weight Percent		
	JP-8	JP-8/2040 Solvent	JP-8/Mineral Seal Oil
Paraffins	46.3	35.4	48.4
Cycloparaffins	32.8	25.0	31.1
Dicycloparaffins	5.8	4.3	5.9
Tricycloparaffins	0.9	0.7	0.8
Alkylbenzenes	7.5	14.3	7.9
Indans and Tetralins	3.9	4.5	3.3
Indenes	0.9	0.6	0.6
Naphthalene	-	4.5	0.6
Naphthalenes	1.9	10.6	1.4
Acenaphthenes	-	0.04	-
Acenaphthylenes	-	-	-
Tricyclic aromatics	-	0.05	-

TABLE 75. DENSITY AND KINEMATIC VISCOSITY OF JP-4 FUELS

Density and Kinematic Viscosity of JP-4 Fuels

Temperature (°F)	Density (g/cc)		Kinematic Viscosity (centistokes)	
	8-24-77	Tank B-11	8-24-77	Tank B-11
0	0.7833	0.7879	1.758	1.850
77	0.7490	0.7540	0.913	0.949
100	0.7384	0.7441	0.792	0.816

TABLE 76. SURFACE TENSION AND VAPOR PRESSURE OF JP-4 FUELS

Temperature (°F)	Surface Tension (Dyne cm^{-1})		Vapor Pressure (Torr)	
	8-24-77	Tank B-11	8-24-77	Tank B-11
32	25.42	26.12	23	19
70	23.60	24.02	61	47
100	22.20	22.17	119	92

TABLE 77. BOILING POINT DISTRIBUTION
(ASTM D2887)

Percent Recovered	JP-4, Tank B-11 (Temperature) °C	°F	JP-4, 8-24-77 (Temperature) °C	°F
0.5 (initial boiling point)	26	78.8		73.5
5.0	69	156	61	142
10.0	89	192	75	167
20.0	103	217	98	207
30.0	119	246	117	242
40.0	134	273	127	261
50.0	153	307	151	304
60.0	178	352	170	338
70.0	199	390	189	372
80.0	218	424	211	412
90.0	237.5	459	235	455
95.0	252	485	252	480
99.5 (end point)	279	534	275	527

TABLE 78. HEAT OF COMBUSTION

	Gross, BTU/lb	Net, BTU/lb
JP-4, Tank B-11	20,046	
	20,031	
	Average 20,039	18,717
JP-4, 8-24-77	20,092	
	20,089	
	Average 20,091	18,767

TABLE 79. HYDROCARBON-TYPE DISTRIBUTION

Compound Type	Volume Percent JP-4, 8-24-77	Volume Percent JP-4, Tank B-11
Paraffins	60.5	62.1
Monocycloparaffins	24.6	21.4
Dicycloparaffins	4.3	5.3
Alkylbenzenes	8.5	8.7
Indans & Tetralins	1.6	1.5
Naphthalenes	0.5	1.0
Average Carbon Number	8.7	9.5

4. CHARACTERIZATION OF MODIFIED JP-4 FUEL

A number of analyses have been conducted on a sample of JP-4 which was modified by the addition of 2040 aromatic solvent. These analyses were required to support combustion test programs which were being conducted with this fuel.

Density, kinematic viscosity, surface tension and vapor pressure were determined as a function of temperature. Viscosity measurements were conducted according to ASTM method D445. Vapor pressure was determined using the apparatus described in Appendix 2. Data for these four properties are presented in Table 80. Equations for calculation of these properties at other temperatures are also given in that table. Heat of combustion was determined by the oxygen bomb calorimeter according to ASTM D240. The results of duplicate determinations are presented in Table 81.

Boiling point distribution of the modified JP-4 was determined by gas chromatography as described in ASTM D2887. Data are presented in Table 82 and plotted in Figure 61.

Hydrocarbon-type distribution was determined by mass spectrometry. The method ordinarily used for JP-4 was modified to accommodate the higher boiling components present in the 2040 solvent. Results are shown in Table 83.

Elemental analyses were obtained by submitting the sample to three independent microanalytical laboratories. The laboratories are:

Lab A	Sanda, Inc., Philadelphia, Pa.
Lab B	Galbraith Laboratories, Knoxville, Tenn.
Lab C	Schwarzkopf Microanalytical Laboratory, Woodside, N.Y.

TABLE 80. VARIOUS PROPERTIES OF JP-4/2040 SOLVENT AS A FUNCTION OF TEMPERATURE

Temperature, °F	Density (d), g/cc	Viscosity, centistokes	Surface Tension (γ_1), dynes cm^{-1}	Vapor Pressure (P), torr
0	0.8559	2.510	27.97	17.5
50	-	-	25.82	-
77	0.8213	1.144	24.95	69.0
100	0.8113	0.961	23.65	96.5

Equations

$d = -0.000446\ T_{°F} + 0.8556$

$\gamma = -0.04339\ T_{°F} + 27.99$

$\log P = -\frac{1050.1}{T_{°K}} + 5.3610$

TABLE 81. HEAT OF COMBUSTION OF JP-4/2040 BLEND

Gross		Net	
BTU/lb	Cal/gram	BTU/lb	Cal/gram
18,765			
18,785			
Av. 18,775	10,430	17,819	9,899

TABLE 82. BOILING POINT DISTRIBUTION DATA OF JP-4/2040

Percent Recovered	°C	°F
0.5 (initial boiling point)	-2	28
5	63	145
10	80	176
20	111	232
30	136	277
40	168	334
50	190	374
60	210	410
70	230	446
80	254	489
90	275	527
95	291	556
99.5 (end point)	334	633

TABLE 83. DISTRIBUTION OF HYDROCARBON TYPES IN JP-4/2040

Distribution of Hydrocarbon Types in JP-4/2040

Compound Type	Volume Percent
Paraffins	47.2
Monocycloparaffins	15.8
Dicycloparaffins	4.0
Alkylbenzenes	15.2
Indanes	2.8
Naphthalenes	14.9

Data are presented in Table 84. Analyses of the starting JP-4 fuel are included in that table.

TABLE 84. ELEMENTAL ANALYSES

Sample	Lab A		Lab B		Lab C	
	C	H	C	H	C	H
JP-4	85.47	14.53	85.34	14.66	85.40	14.66
	85.43	14.57	85.57	14,50	85.44	14.47
Average	85.45	14.55	85.45	14.58	85.42	14.57
JP-4/2040	88.05	11.95	85.22	11.66	87.43	12.48
	87.81	12.19	85.09	11.80	87.59	12.37
Average	87.93	12.07	85.16*	11.73	87.51	12.42

*Values were checked with Laboratory B and confirmed to be as determined.

5. CHARACTERIZATION OF JP-4, JP-8 and MODIFIED FUELS

A number of fuels, consisting of JP-4, JP-8 and these fuels blended with other stock, were characterized in further support of Air Force combustion studies. Density, surface tension and vapor pressure were determined as a function of temperature, and simulated distillations by gas chromatography (ASTM D2887) were conducted for each specimen. Viscosity, heat of combustion and hydrocarbon type analysis data were al') recorded for some specimens.

Blending stocks consisted of either a mixture of xylenes, 2040 aromatic solvent or Gulf mineral seal oil. The numeral after the second hyphen in the sample numbers, shown in Tables 86 through 101, designates the fuel type as JP-4 or JP-8. The letters following the numeral indicate the blending stock as either the xylenes mixture (XY), aromatic solvent (AR) or Gulf mineral seal oil (GM). Straight unmodified fuels are designated by (ST). All blends were prepared prior to their shipment to MRC for testing. The number following the third hyphen indicates the hydrogen content of the fuel or blend. The final number indicates the individual specimen.

A detailed characterization of the xylenes mixture and 2040 aromatic solvent were presented in subsection 1 of this section. Elemental analyses were obtained for Gulf mineral seal oil and for RJ-1, which was also considered as a potential blending stock to increase boiling range. These data are presented in Table 85.

Density data for the test fuels are presented in Table 86, surface tension in Table 87, vapor pressure in Table 88, simulated distillation in Tables 89 through 98, viscosity in Table 99, and heat of combustion in Table 100, and hydrocarbon type analysis data for three specimens in Table 101.

TABLE 85. ELEMENTAL ANALYSES

Laboratory	RJ-1		Gulf Mineral Seal Oil	
	Weight Percent			
	Carbon	Hydrogen	Carbon	Hydrogen
Lab A	86.54	13.46	85.85	14.14
	86.56	13.43	85.81	14.18
Averages	86.55	13.45	85.83	14.16
Lab B	86.29	13.79	86.33	13.73
	86.40	13.60	86.33	13.86
Averages	86.34	13.69	86.32	13.79
Grand Mean Value	84.40	13.57	86.07	13.93

Lab A Sanda, Inc., Philadelphia

Lab B Galbraith Laboratories, Knoxville

TABLE 86. DENSITY OF TEST FUELS AS A FUNCTION OF TEMPERATURE

Sample Number	grams/cm³ 32°F (°C)	70°F (21.1°C)	100°F (37.8°C)
GE/TJ-78-4ST-14.5-02	0.7878	0.7532	0.7443
GE/TJ-78-4ST-14.5-03	0.7879	0.7542	0.7441
GE/TJ-78-4ST-14.5-04	0.7882	0.7540	0.7440
GE/TJ-78-4ST-14.5-05	0.7881	0.7538	0.7435
GE/TJ-78-4ST-14.5-06	0.7885	0.7546	0.7443
GE/TJ-78-4ST-14.5-07	0.7883	0.7540	0.7440
GE/TJ-78-4ST-14.5-08	0.7883	0.7545	0.7439
GE/TJ-78-4ST-14.5-09	0.7746	0.7584	0.7453
GE/TJ-78-4ST-14.5-10	0.7750	0.7586	0.7453
GE/TJ-78-4ST-14.5-11	0.7746	0.7580	0.7448
GE/TJ-78-4ST-14.5-12	0.7750	0.7587	0.7456
GE/TJ-78-4ST-14.5-13	0.7744	0.7583	0.7451
GE/TJ-78-8ST-14.0-02	0.8326	0.8008	0.7914
GE/TJ-78-8ST-14.0-03	0.8327	0.8008	0.7916
GE/TJ-78-8ST-14.0-04	0.8326	0.8006	0.7912
GE/TJ-78-8ST-14.0-05	0.8326	0.8013	0.7918
GE/TJ-78-8ST-14.0-06	0.8326	0.8010	0.7912
GE/TJ-78-8ST-14.0-07	0.8191	0.8038	0.7915
GE/TJ-78-8ST-14.0-08	0.8187	0.8034	0.7911
GE/TJ-78-8ST-14.0-09	0.8189	0.8038	0.7919
GE/TJ-78-8ST-14.0-10	0.8177	0.8023	0.7900
GE/TJ-78-8GM-14.0-02	0.8335	0.8026	0.7932
GE/TJ-78-8GM-14.0-03	0.8338	0.8023	0.7933
GE/TJ-78-8GM-14.0-04	0.8343	0.8031	0.7933
GE/TJ-78-8GM-14.0-05	0.8344	0.8032	0.7937
GE/TJ-78-8GM-14.0-06	0.8335	0.8021	0.7931
GE/TJ-78-8GM-14.0-07	0.8206	0.8055	0.7953
GE/TJ-78-8GM-14.0-08	0.8208	0.8056	0.7936
GE/TJ-78-8GM-14.0-09	0.8208	0.8056	0.7935
GE/TJ-78-8GM-14.0-10	0.8202	0.8052	0.8933
GE/TJ-78-8XY-13.0-01	0.8338	0.8179	0.8052
GE/TJ-78-8XY-12.0-01	0.8482	0.8319	0.8188
GE/TJ-78-8AR-12.0-01	0.8725	0.8569	0.8445

TABLE 87. SURFACE TENSION OF TEST FUELS AS A FUNCTION OF TEMPERATURE

Sample Number	dyne/cm^{-1}		
	32°F	70°F	100°F
GE/TJ-78-4ST-14.5-02	25.1	23.1	21.7
GE/TJ-78-4ST-14.5-03	24.9	22.8	21.6
GE/TJ-78-4ST-14.5-04	25.1	22.8	21.4
GE/TJ-78-4ST-14.5-05	25.0	23.4	22.6
GE/TJ-78-4ST-14.5-06	25.1	23.0	21.8
GE/TJ-78-4ST-14.5-07	25.1	23.4	22.3
GE/TJ-78-4ST-14.5-08	25.0	22.9	21.8
GE/TJ-78-4ST-14.5-09	24.6	22.9	21.4
GE/TJ-78-4ST-14.5-10	25.0	23.0	21.4
GE/TJ-78-4ST-14.5-11	24.9	23.0	21.4
GE/TJ-78-4ST-14.5-12	24.9	23.0	21.5
GE/TJ-78-4ST-14.5-13	24.8	22.9	21.3
GE/TJ-78-8ST-14.0-02	28.2	26.3	25.1
GE/TJ-78-8ST-14.0-03	28.4	26.4	25.1
GE/TJ-78-8ST-14.0-04	28.5	26.5	25.3
GE/TJ-78-8ST-14.0-05	27.4	25.9	25.0
GE/TJ-78-8ST-14.0-06	28.7	26.5	25.5
GE/TJ-78-8ST-14.0-07	28.1	25.9	24.3
GE/TJ-78-8ST-14.0-08	27.0	26.0	24.4
GE/TJ-78-8ST-14.0-09	28.0	25.9	24.3
GE/TJ-78-8ST-14.0-10	27.6	25.6	24.1
GE/TJ-78-8GM-14.0-02	28.5	26.6	25.5
GE/TJ-78-8GM-14.0-03	28.6	26.7	25.5
GE/TJ-78-8GM-14.0-04	27.6	26.2	25.3
GE/TJ-78-8GM-14.0-05	28.5	26.4	25.0
GE/TJ-78-8GM-14.0-06	28.3	26.4	25.2
GE/TJ-78-8GM-14.0-07	27.8	26.4	24.2
GE/TJ-78-8GM-14.0-08	27.9	26.3	24.7
GE/TJ-78-8GM-14.0-09	28.4	26.3	24.7
GE/TJ-78-8GM-14.0-10	27.9	25.9	24.3
GE/TJ-78-8XY-12.0-01	29.2	27.2	26.5
GE/TJ-78-8XY-13.0-01	28.9	26.3	25.3
GE/TJ-78-8AR-12.0-01	29.8	28.1	26.7

TABLE 88. VAPOR PRESSURE OF TEST FUELS AS A FUNCTION OF TEMPERATURE

Sample Number	torr		
	32°F (0°C)	70°F (21°C)	100°F (38°C)
GE/TJ-78-4ST-14.5-02	34	74	127
GE/TJ-78-4ST-14.5-03	30	70	126
GE/TJ-78-4ST-14.5-04	31	72	124
GE/TJ-78-4ST-14.5-05	39	69	122
GE/TJ-78-4ST-14.5-06	32	73	126
GE/TJ-78-4ST-14.5-07	28	67	119
GE/TJ-78-4ST-14.5-08	29	70	121
GE/TJ-78-4ST-14.5-09	24	65	110
GE/TJ-78-4ST-14.5-10	25	70	118
GE/TJ-78-4ST-14.5-11	24	68	115
GE/TJ-78-4ST-14.5-12	25	72	120
GE/TJ-78-4ST-14.5-13	24.5	70	118
GE/TJ-78-8ST-14.0-02	10.5	14.5	19
GE/TJ-78-8ST-14.0-03	10	14.5	18.5
GE/TJ-78-8ST-14.0-04	10	14	18.5
GE/TJ-78-8ST-14.0-05	9.5	13	17.5
GE/TJ-78-8ST-14.0-06	10	14.5	19
GE/TJ-78-8ST-14.0-07	7.5	12	16
GE/TJ-78-8ST-14.0-08	8	13	18.5
GE/TJ-78-8ST-14.0-09	8	12.5	17
GE/TJ-78-8ST-14.0-10	8.5	12.5	18
GE/TJ-78-8GM-14.0-02	7	9	11.5
GE/TJ-78-8GM-14.0-03	7.5	9.5	19.5
GE/TJ-78-8GM-14.0-04	8	10	12
GE/TJ-78-8GM-14.0-05	7	9	11
GE/TJ-78-8GM-14.0-06	7.5	9	11
GE/TJ-78-8GM-14.0-07	5	8	11.5
GE/TJ-78-8GM-14.0-08	5	8	11
GE/TJ-78-8GM-14.0-09	6	10	12.5
GE/TJ-78-8GM-14.0-10	8.5	13	18
GE/TJ-78-8AR-12.0-01	4.2	7.5	11.5
GE/TJ-78-8XY-12.0-01	3.6	8.2	14.5
GE/TJ-78-8XY-13.0-01	4.0	9.1	16.3

TABLE 89. GAS CHROMATOGRAPHIC SIMULATED DISTILLATIONS OF TEST FUELS GE/TJ-78-4ST-14.5-02 TO -08

Percent Recovered	-02		-03		-04		-05		-06		-07		-08	
	°C	°F	°C	°F	°C	°F	°C	°F	°C	°F	°C	°F	°C	°F
0.5, IBP	27	81	29	84	28	82	28	82	28	82	29	84	29	84
1	35	95	34	93	34	93	33	91	36	97	35	95	35	95
5	68	154	67	153	67	153	66	151	68	154	68	154	67	153
10	88	190	87	189	87	189	87	189	88	190	88	190	88	190
20	102	216	100	212	100	212	99	210	102	216	102	216	101	214
30	117	243	116	241	117	243	116	241	117	243	117	243	117	243
40	131	268	131	268	128	262	126	259	131	268	131	268	131	268
50	150	302	150	302	147	297	144	291	150	302	149	300	150	302
60	174	345	173	343	172	342	171	340	174	345	174	345	174	345
70	196	385	195	383	195	383	194	381	196	385	196	385	195	383
80	216	421	216	421	215	419	215	419	218	424	216	421	216	421
90	236	457	235	455	235	455	234	453	235	455	235	455	235	455
95	250	482	250	482	249	480	250	482	250	482	250	482	250	482
99	268	514	268	514	268	514	266	511	268	514	268	514	268	514
99.5	276	529	273	523	271	520	271	520	273	523	273	523	271	520

TABLE 90. GAS CHROMATOGRAPHIC SIMULATED DISTILLATIONS OF TEST FUELS (ASTM D2887)
GE/TJ-78-4ST-14.5-09 TO -13

Percent Recovered	-09		-10		-11		-12		-13	
	°C	°F	°C	°F	°C	°F	°C	°F	°C	°F
0.5, IBP	26	78.8	27	80.6	27	30.6	27	80.6	28	82.4
1	32	89.6	34	93.2	34	93.2	36	96.8	36	96.8
5	69	156.2	68	154.4	68	154.4	68	154.4	69	156.2
10	89	192.2	88	190.4	88	190.4	88	190.4	89	192.2
20	105	221.0	104	219.2	105	221.0	105	221.0	106	222.8
30	122	251.6	119	246.2	119	246.2	119	246.2	119	246.2
40	139	282.2	135	275.0	136	276.8	136	276.8	137	278.6
50	159	318.2	156	312.8	156	312.8	157	314.6	158	316.4
60	182	359.6	180	356.0	180	356.0	180	356.0	181	357.8
70	202	395.6	200	392.0	200	392.0	200	392.0	200	392.0
80	220	428.0	218	424.4	218	424.4	219	426.2	219	426.2
90	239	462.2	237	458.6	237	458.6	238	460.4	239	462.2
95	252	485.6	251	483.8	251	483.8	251	483.8	251	483.8
99	270	518.0	271	519.8	271	519.8	271	519.8	271	519.8
99.5, FBP	280	536.0	283	541.4	283	541.4	283	541.4	283	541.4

TABLE 91. GAS CHROMATOGRAPHIC SIMULATION DISTILLATION OF SAMPLES GE/TJ-78-8ST-14.0-02 TO -06

Percent Recovered	02		03		04		05		06	
	°C	°F	°C	°F	°C	°F	°C	°F	°C	°F
0.5, IBP	104	221	108	226	109	229	110	230	112	234
1	117	243	120	248	117	243	122	252	122	252
5	152	306	153	307	152	306	153	307	154	309
10	166	331	165	329	165	329	166	331	166	331
20	180	356	179	354	180	356	180	356	180	356
30	194	381	195	383	193	379	192	378	195	383
40	203	397	203	397	202	396	203	397	203	397
50	216	421	215	419	215	419	216	421	215	419
60	227	441	226	439	226	439	227	441	226	439
70	237	459	237	459	236	457	236	457	235	455
80	253	487	252	486	252	486	252	486	252	486
90	270	518	269	516	268	514	268	514	268	514
95	287	549	282	540	280	536	282	540	282	540
99	303	577	304	579	301	574	303	577	301	574
99.5	312	594	316	598	311	592	312	594	310	590

TABLE 92. GAS CHROMATOGRAPHIC SIMULATED DISTILLATIONS OF TEST FUELS (ASTM D2887)
GE/TJ-78-8ST-14.0-07 TO -10

Percent Recovered	-07		-08		-09		-10	
	°C	°F	°C	°F	°C	°F	°C	°F
0.5, IBP	102	215.6	102	215.6	106	222.8	94	201.2
1	116	240.8	118	244.4	121	249.8	111	231.8
5	150	302.0	151	303.8	134	273.2	151	303.8
10	164	327.2	166	330.8	167	332.6	166	330.8
20	179	354.2	180	356.0	180	356.0	181	357.8
30	192	377.6	194	381.2	194	381.2	198	388.4
40	204	399.2	204	399.2	204	399.2	205	401.0
50	216	420.8	216	420.8	216	420.8	219	426.2
60	228	442.4	229	444.2	227	440.6	229	444.2
70	239	462.2	237	458.6	238	460.4	239	462.2
80	252	485.6	251	483.8	251	483.8	253	487.4
90	271	519.8	268	514.4	268	514.4	270	518.0
95	286	546.8	282	539.6	282	539.6	283	541.4
99	319	606.2	307	584.6	307	584.6	305	581.0
99.5, FBP	327	620.6	321	609.8	319	606.2	315	599.0

TABLE 93. GAS CHROMATOGRAPHIC SIMULATED DISTILLATION OF SAMPLES GE/TJ-78-8GM-14.0-02 TO -06

Percent Recovered	02		03		04		05		06	
	°C	°F	°C	°F	°C	°F	°C	°F	°C	°F
0.5, IBP	110	230	105	221	105	221	108	226	102	216
1	125	257	118	244	117	243	118	244	115	239
5	157	315	154	309	154	309	155	311	152	306
10	168	334	168	334	168	334	168	334	166	331
20	183	361	182	360	182	360	183	361	182	360
30	196	385	196	385	196	385	195	383	196	385
40	210	410	210	410	210	410	210	410	208	406
50	221	430	221	428	220	428	220	428	220	428
60	235	455	234	453	234	453	235	455	234	453
70	250	482	249	480	250	482	249	480	249	480
80	267	513	266	511	268	514	267	513	266	511
90	291	556	290	554	293	559	291	556	289	552
95	306	583	305	581	309	588	308	586	304	579
99	333	631	333	631	339	642	338	640	331	628
99.5	345	653	345	653	349	660	354	668	344	651

TABLE 94. GAS CHROMATOGRAPHIC SIMULATED DISTILLATIONS OF TEST FUELS (ASTM D2887)
GE/TJ-78-8GM-14.0-07 TO -10

Percent Recovered	-07		-08		-09		-10	
	°C	°F	°C	°F	°C	°F	°C	°F
0.5, IBP	116	240.8	115	239.0	114	237.2	104	219.2
1	127	260.6	125	257.0	125	257.0	118	244.4
5	157	314.6	157	314.6	156	312.8	149	300.2
10	169	336.2	169	336.2	168	334.4	165	329.0
20	182	359.6	184	363.2	183	361.4	181	357.8
30	196	384.8	196	384.8	196	384.8	197	386.6
40	211	411.8	211	411.8	210	410.0	210	410.0
50	224	435.2	222	431.6	222	431.6	222	431.6
60	235	455.0	235	455.0	235	455.0	235	455.0
70	251	483.8	250	482.0	250	482.0	251	483.8
80	268	514.4	267	512.6	267	512.6	269	516.2
90	291	555.8	290	554.0	291	555.8	296	564.8
95	306	582.8	306	582.8	307	584.6	313	595.4
99	333	631.4	332	629.6	335	635.0	342	647.6
99.5, FBP	347	656.6	342	647.6	347	656.6	349	660.2

TABLE 95. GAS CHROMATOGRAPHIC SIMULATED DISTILLATIONS OF TEST FUELS (ASTM D2887) GE/TJ-78 SERIES

Percent Recovered	8XY-12.0-01 °C	8XY-12.0-01 °F	8XY-13.0-01 °C	8XY-13.0-01 °F	8AR-12.0-01 °C	8AR-12.0-01 °F
0.5 (Initial B.P.)	104	219	120	248	118	244
5	138	280	139	282	161	322
10	140	284	145	293	173	343
20	150	302	161	322	190	374
30	160	320	170	338	202	396
40	166	331	183	361	213	415
50	171	340	196	385	226	439
60	188	370	212	414	230	446
70	207	405	228	442	239	462
80	228	442	241	466	251	484
90	253	487	261	502	269	516
95	270	518	276	529	284	543
99.5 (End Point)	328	622	309	588	317	603

TABLE 96. GAS CHROMATOGRAPHIC SIMULATED DISTILLATIONS OF TEST FUELS GE/TJ-78 SERIES

Percent recovered	8XY-12.0-02 °C	8XY-12.0-02 °F	8XY-12.0-03 °C	8XY-12.0-03 °F	8XY-12.0-04 °C	8XY-12.0-04 °F
0.5, IBP	124	255	124	255	116	241
1	135	275	134	273	131	268
5	138	280	137	279	137	279
10	142	288	141	286	142	288
20	151	304	151	304	151	304
30	161	322	161	322	161	322
40	167	333	166	331	168	334
50	177	351	174	345	179	354
60	194	381	192	378	195	383
70	214	417	213	415	215	419
80	232	450	231	448	233	451
90	253	487	253	487	256	493
95	270	518	270	518	272	522
99	299	570	303	577	303	577
99.5, FBP	316	601	321	610	320	608

TABLE 97. GAS CHROMATOGRAPHIC SIMULATED DISTILLATIONS OF TEST FUELS (ASTM D2887)

Percent recovered	8XY-13.0-02 °C	8XY-13.0-02 °F	8XY-13.0-03 °C	8XY-13.0-03 °F	8XY-13.0-04 °C	8XY-13.0-04 °F	8XY-13.0-05 °C	8XY-13.0-05 °F
0.5, IBP	116	241	116	241	115	239	112	234
1	130	266	130	266	127	261	123	253
5	140	284	138	280	138	280	138	280
10	145	293	144	291	143	289	143	289
20	162	323	161	322	160	320	160	320
30	172	342	170	338	170	338	169	336
40	186	367	185	365	184	363	184	363
50	200	392	198	388	198	388	198	388
60	215	419	214	417	214	417	213	415
70	229	444	228	442	227	441	227	441
80	244	471	243	469	242	468	243	469
90	262	504	261	502	261	502	261	502
95	277	531	276	529	275	527	276	529
99	301	574	300	572	299	570	303	577
99.5, FBP	315	599	316	601	312	594	318	604

TABLE 98. GAS CHROMATOGRAPHIC SIMULATED DISTILLATIONS OF TEST FUELS GE/TJ-78 SERIES

Percent recovered	8AR-12.0-02 °C	8AR-12.0-02 °F	8AR-12.0-03 °C	8AR-12.0-03 °F	8AR-12.0-04 °C	8AR-12.0-04 °F	8AR-12.0-05 °C	8AR-12.0-05 °F
0.5, IBP	119	246	120	248	116	241	120	248
1	131	268	133	271	130	266	132	270
5	161	322	163	325	161	322	162	324
10	172	342	174	345	172	342	172	342
20	188	370	191	376	188	370	189	372
30	201	394	203	393	201	394	202	396
40	212	414	215	419	212	414	213	415
50	226	439	225	437	225	437	226	439
60	232	450	235	455	230	446	230	446
70	242	468	244	471	241	466	240	464
80	252	486	254	489	251	484	251	484
90	270	518	271	520	268	514	268	514
95	285	545	285	545	281	538	281	538
99	335	635	320	608	313	595	310	590
99.5 FBP	352	666	344	651	340	644	338	640

TABLE 99. KINEMATIC VISCOSITY AS A FUNCTION OF TEMPERATURE (ASTM D445)

Sample Number	centistokes		
	0°F(-17.8°C)	77°F(25°C)	100°F(37.8°C)
GE/TJ-78-4ST-14.5-09	1.877	0.961	0.827
GE/TJ-78-4ST-14.5-10	1.885	0.959	0.825
GE/TJ-78-4ST-14.5-11	1.877	0.957	0.823
GE/TJ-78-4ST-14.5-12	1.881	0.964	0.829
GE/TJ-78-4ST-14.5-13	1.882	0.960	0.827
GE/TJ-78-8ST-14.0-07	5.242	1.894	1.538
GE/TJ-78-8ST-14.0-08	5.192	1.883	1.530
GE/TJ-78-8ST-14.0-09	5.247	1.896	1.537
GE/TJ-78-8ST-14.0-10	5.043	1.850	1.502
GE/TJ-78-8GM-14.0-07	6.257	2.127	1.707
GE/TJ-78-8GM-14.0-08	6.207	2.120	1.703
GE/TJ-78-8GM-14.0-09	6.245	2.127	1.708
GE/TJ-78-8GM-14.0-10	6.129	2.102	1.688
GE/TJ-78-8XY-13.0-01	3.557	1.464	1.221
GE/TJ-78-8XY-12.0-01	2.628	1.188	1.004
GE/TJ-78-8AR-12.0-01	5.368	1.873	1.513

TABLE 100. HEAT OF COMBUSTION OF TEST FUELS (D240-64)

Sample	Gross, BTU/lb	Net, BTU/lb
GE/TJ-78-4ST-14.5-09	20,117	
	20,130	
	Avg 20,124	18,812
GE/TJ-78-4ST-14.5-10	20,090	
	20,113	
	Avg 20,101	18,812
GE/TJ-78-4ST-14.5-11	20,135	
	20,113	
	Avg 20,124	18,816
GE/TJ-78-4ST-14.5-12	20,123	
	20,125	
	Avg 20,124	18,816
GE/TJ-78-4ST-14.5-13	20,104	
	20.093	
	Avg 20,099	18,789
GE/TJ-78-8ST-14.0-07	19,893	
	19,874	
	Avg 19,884	18,582
GE/TJ-78-8ST-14.0-08	19,843	
	19,825	
	Avg 19,834	18,565
GE/TJ-78-8ST-14.0-09	19,805	
	19,815	
	Avg 19,810	18,537
GE/TJ-78-8ST-14.0-10	19,817	
	19,855	
	Avg 19,836	18,566
GE/TJ-78-8GM-14.0-07	19,846	
	19,885	
	Avg 19,866	18,591
GE/TJ-78-8GM-14.0-08	19,831	
	19,777	
	Avg 19,804	18,527
GE/TJ-78-8GM-14.0-09	19,843	
	19,864	
	Avg 19,854	18,577
GE/TJ-78-8GM-14.0-10	19,858	
	19,841	
	Avg 19,850	18,579
GE/TJ-78-8AR-12.0-01	19,130	
	19,173	
	Avg 19,152	18,057
GE/TJ-78-8XY-12.0-01	19,178	
	19,209	
	Avg 19,194	18,099
GE/TJ-78-8XY-13.0-01	19,495	
	19,495	
	Avg 19,495	18,309

TABLE 101. HYDROCARBON TYPE ANALYSES FOR FUELS CODED GF/TJ-78

Compound type	Volume, percent		
	8XY-12.01	8XY-13.01	8XY-12.01
Paraffins	25.7	35.6	29.9
Monocycloparaffins	21.5	30.6	26.4
Dicycloparaffins	1.9	2.3	1.7
Alkylbenzenes	49.9	28.9	11.7
Indans	none detected	1.0	5.7
Naphthalene	1.0	1.6	24.6

SECTION V

HYDROCARBON TYPE ANALYSIS METHODOLOGY SURVEY

The hydrocarbon composition of a jet turbine fuel not only affects engine performance and power output, but cost of operation and engine life as well. Correlations between combustion behavior and fuel composition are possible only if suitable methods for determining fuel composition are available. Fuels are complex mixtures of hydrocarbons of many varying types, thus a complete analysis to determine every component of a fuel is rarely practical. Since hydrocarbons within a class behave similarly, a fuel can be characterized by determining its composition in terms of the various constituent compound types or classes.

A critical survey of the methods for hydrocarbon type analysis was felt to be urgently needed to provide an insight into how the many established methods differ and to determine which ones provide data that best correlate with fuel properties.

Methods may vary from those which simply provide a measure of total aromatic and aliphatic hydrocarbons, to those which give a number of sub types for each of these compound classes.

A literature review was conducted with the intent of producing a critical look at some of the current hydrocarbon-type analytical methods as they might apply to jet aircraft fuels. The review, of necessity, does not include all such methods of analysis; such a work would fill volumes.

A major review on hydrocarbon analysis, which was published by the American Society for Testing Materials (ASTM) (10) described the existing state of hydrocarbon analysis technology

through the year 1964. Methods discussed in that work will be included only when needed as a background for discussion of advances in methodology and techniques.

The various analytical approaches are discussed in the following subsections.

1. MASS SPECTROMETRY

Except for the widely used displacement chromatographic method known as Fluorescent Indicator Analysis (FIA), mass spectrometry has perhaps been the technique most used by petroleum chemists for hydrocarbon type analysis. As such, it has played an important role in the petroleum industry over the past 25 years. While now being supplemented to a great extent by other rapid analytical methods, the technique still finds extensive application to the analysis of hydrocarbon types in fuels and feedstocks. Mass spectrometry provides data that can be general for hydrocarbons within a give class, yet fairly specific for individual compound classes. The mass spectrum of a mixture is the sum of the mass spectra of each individual component. Thus almost all mass spectral hydrocarbon type calculations consist of summing individual mass spectral lines which are characteristic of each compound type. A matrix of n equations and n unknowns is constructed, where n is the number of different compound types being determined. Simultaneous solution of these equations gives a quantitative measure of each compound type present. An average carbon number can be calculated for each component type, thus giving a reasonable compositional profile for the sample. The first hydrocarbon-type analysis by this approach was developed for the analysis of gasoline by R. A. Brown in 1951 (11). The method allowed the determination of paraffins, cycloparaffins, mono-olefins, aromatics and a group of compounds designated as a "coda" type, consisting of total cyclomono-olefins, diolefins and

acetylenes. Brown used data for some 500 gasoline specimens to develop the technique. Similar methods for other low boiling distillates were soon developed by other workers (12, 13). The approach was later improved substantially by application of the concept of total ionization (14, 15) which allowed calibration data for the various hydrocarbon types to be related directly to volume percent.

Mass spectral hydrocarbon type analyses have been developed to cover a broad range of sample types and boiling ranges. Most of the methods can be seriously affected by the presence of significant amounts of non-hydrocarbons unless these are included in the matrix calculation. Hastings (16) determined 12 aromatic compound types in a procedure in which he includes three thiopheno types. Robinson and Cook (17) developed a procedure for determining up to 21 compound types in petroleum aromatic fractions, including 12 aromatic types, three thiopheno types and 6 unidentified groups. Inclusion of the unidentified components avoided the difficulty sometimes encountered in methods which describe composition in terms of a fixed number of named types. That method is applicable to a wide range of samples. A more general method was later developed (18) by the same investigator to determine up to 25 saturate and aromatic compound types in petroleum fractions. The entire composition of any fraction boiling in the 200-1100°F range is accounted for in terms of four saturated hydrocarbon types, 12 aromatic types, 3 thiopheno types, and 6 unidentified aromatic groups. The method was shown to give consistent results on a wide variety of samples.

Methods which are relevant to aircraft fuels have been adopted as standard ASTM methods: D2789-81 is suitable for JP-4 and D2559 for kerosene range fuels. The latter method requires a preliminary separation of the sample into aromatic and saturated fractions by a column chromatographic technique such as that described in ASTM D2425.

The mass spectrometric methods as discussed above are not without their limitations. Significant amounts of non-hydrocarbon materials may be present in a fuel and may result in a specific and unavoidable interference. For example, petroleum aromatic fractions often include dibenzofurans (19, 20) a compound group which is, in most cases, indistinguishable from acenaphthenes (21). Other similar interferences are probable, particularly in higher boiling fractions.

The availability of gas chromatographic/mass spectrometric/on-line data systems has made possible the acquisition of highly detailed information on the composition of extremely complex mixtures of organic substances. By this technique, spectra can be respectively recorded, manipulated, monitored and interrogated in real-time. Specific questions concerning fuel composition can often be answered by the technique of specifc ion monitoring (SIM), in which the total-ion plot (chromatogram) is searched for the presence of specific ions which are characteristic of the compound or compound-type which is sought. While this approach is not one of compound type analyis, it deserves mention in any discussion of mass spectrometric analysis of hydrocarbons.

2. NUCLEAR MAGNETIC RESONANCE

Nuclear magnetic resonance has found increasing application for the compositional characterization of hydrocarbon materials, particularly residuals and crude oils which pose difficult separation problems. Many of these techniques are applicable to the analysis of aircarft fuels. The applications generally produce information on bulk properties and structural characteristics, rather than identification of specific compounds. In proton resonance spectrometry, nuclei of hydrogen atoms can be differentiated depending on the type of atom to which they are attached and the type of

atom or functional group bonded to the adjacent atom. Thus hydrogen atoms attached, for example, to carbons or on an aromatic ring, or to olefinic carbon, can be distinguished from hydrogen atoms in other groupings. The measured hydrogen distributions can then be used to deduce the structures of the various carbon skeletons. Carbon-13, which occurs naturally in carbonaceous materials at about 1.1%, can be used to record magnetic resonance spectra of skeletal carbons directly.

Proton Resonance

R. B. Williams (22) conducted a structural characterization of petroleum hydrocarbons using proton magnetic resonance. His data, which were supplemented by molecular weight information and elemental analysis, were used to characterize paraffins, aromatics and olefins in petroleum. The method required that the sample be separated into aromatic, olefinic and saturate fractions with NMR measurements being obtained on each portion. For the aromatic fraction, an aromatic hydrogen band, an alpha-alkyl hydrogen band, and an alkyl hydrogen band made up of less well-resolved bands due to other aliphatic types, were recorded. In the saturate fraction, partial resolution between cyclic methylene, acyclic methylene and methyl hydrogens was great enough to obtain an indication of the relative concentration of types from simple uncorrected peak height measurements. For the aromatic fraction, data were used to calculate the number of alkyl and aromatic ring carbons and the amount of alkyl substitution on aromatic rings. The average number of aromatic rings per nucleus or per molecule and the number of carbon atoms per alkyl group could also be determined.

A proton resonance method developed by Brown and Ladner for coal-like materials could be equally well applied to petroleum fuels (23). Preliminary separation into aromatic and paraffinic fractions is not necessary in this case. As in the previous method,

NMR integrated band intensities for the aromatic, α-alkyl and other alkyl hydrogens are used, along with elemental analysis data. Aromaticity, $(f)_a$, the molar ratio of aromatic carbon to total carbon in the sample, can be calculated by the equation:

$$(f)_a = \frac{C/H - H_\alpha^*/x - H_o^*/y}{C/H}$$

where C/H is the atomic ratio of carbon to hydrogen from the elemental analysis, x and y are the average number of hydrogens per α-alkyl and the remaining alkyl groups, respectively. H_α^* and H_o^* represent the normalized integrated intensities of the α-alkyl and other non-aromatic alkyl hydrogens. In addition to aromaticity, the degree of substitution of the aromatic system, i.e. the fraction of the available aromatic edge atoms occupied by substituents, can be calculated by this method. Since the analytical procedure was developed for coal and similar materials, account was taken of the oxygen present in the specimen. For fuels in which the oxygen content is low, the value for the atomic ratio of oxygen and hydrogen (O/H) would be insignificant in the following equation for the degree of substitution, σ.

$$\sigma = \frac{H_\alpha^* + O/H}{H_\alpha^*/x + O/H + H_{ar}^*} \qquad (6)$$

All terms are as defined above; H_{ar}^* is the function of total hydrogen on aromatic rings.

A method proposed by Clutter et al. (24) for the characterization of aromatic fractions uses a proton resonance spectrum to calculate all of the average parameters determined by Williams' method with no additional information being required for the computations. The fraction of monoaromatic and diaromatic (fused) ring systems, the average molecular formula, and average molecular weight, can be determined from the NMR data. In this method, it is assumed that ring systems are limited to mono-

and diaromatic types. Jet fuels rarely contain more than a small amount of aromatics with more than two rings. It is further assumed that aromatic ring protons are sufficiently separated in the proton resonance spectrum so that the ratio of mono- to diaromatic protons can be measured. Reference NMR data show that this assumption is justified. A third assumption is that the number of substituents in both mono- and diaromatic components is the same. The degree to which this is true is unknown. An obvious advantage of this method is that no supplemental data are required for analysis.

Myers, Stollsteimer and Wims (25) developed an NMR method for determining saturates, aromatics, and olefins in gasoline. Owing to the narrow range of hydrocarbons to which the method is applicable, no supplementary data are required. As with all proton resonance techniques, only carbons containing at least one proton can be detected and counted. Myers et al. developed a weighted ratio of carbons counted to carbons present, for both aromatics and saturates, by considering the individual hydrocarbons and their concentrations in a typical gasoline of known composition. These ratios were then used to correct for uncounted carbon atoms. Similarly, a correction for the olefinic contribution to the paraffinic methine was required because methyl and methylene groups alpha to the carbon-carbon double bonds resonate there. The correction was again based on the typical gasoline composition. The composition of JP-4 fuels varies too much to make their method useful for that fuel.

We have recorded proton NMR spectra for several jet fuels, which were also analyzed by mass spectrometry. By making modifications in the method of Myers, et al., we have been able to largely eliminate the need for assurance that the fuel fits a "typical" composition. This work is discussed later in this section. The major compositional feature which would cause error in the modified method is a high level of polynuclear aromatic hydrocarbons.

These compounds as a class contain abundant carbon atoms having no protons attached. Fortunately, their level in aircraft fuel is usually quite low.

Carbon-13 Resonance

Friedel and Retcofksy (26) as early as 1966 investigated the usefulness of ^{13}C NMR for evaluating aromaticity in petroleum fractions. These authors concluded that ^{13}C NMR data combined with data from other sources, especially proton resonance, could provide an excellent means of structural elucidation.

Knight (27) devised a method of determining the average parameters of aromatic petroleum fractions using a combination of ^{13}C and proton nuclear magnetic resonance.

Clutter et al. (24) further investigated combined ^{13}C and proton resonance and proposed using ^{13}C NMR data for calibrating proton NMR. Additional data required for this method are average molecular weight and elemental analysis. Three characteristic regions of the ^{13}C spectrum, with areas designated, A_1, A_2 and A_3 were measured.

Aromatic and olefinic carbon chemical shifts overlap, but olefinic protons are readily recognized in the proton NMR spectrum. The greater separation in ^{13}C chemical shifts, compared to those of proton resonance, is an asset in structure determinations. Additionally ^{13}C-^{1}H coupling constants can be used to make unambiguous assignments of particular types of carbon atoms.

Utilization of ^{13}C NMR has increased from nearly no applications twelve years ago to the present state of rapid development in that area. This increase is, at least in part, due to the development of fast Fourier transform (FT) techniques and the lower cost of minicomputers and associated hardware. Recent gains in

the quantitative aspects of FT ^{13}C NMR have made the technique attractive for the accurate characterization of fuels. A variety of factors may alter the basic relationship between resonance peak intensity and the number of nuclei at resonance in the FT mode. Of these, the dependence of spin-lattice relaxation recovery times (T_1) on pulse repetition rate, and an effect called nuclear Overhauser enhancement, are the most serious. Paramagnetic decoupling agents have been found which can be added to the sample to allow more rapid repetition rates by decreasing T_1; nuclear Overhauser effects are also suppressed thereby. Another method of avoiding these effects is the use of a gated proton decoupling sequence in which the proton decoupler is on only during the time the ^{13}C signal is monitored.

Shoolery and Budde (28) investigated Fourier Transform ^{13}C NMR for the analysis of crude oil and petroleum products. They observed absorption bands which fell into two well-defined regions, one clearly corresponding to saturate carbons, and the other to aromatic carbons. In the absence of significant quantities of olefinic carbons, integration of these two regions of the ^{13}C spectrum was proposed as a rapid measure of aromatic and saturate carbon.

Other workers have shown the feasibility of using FT ^{13}C NMR, especially in conjunction with proton resonance, to characterize hydrocarbon mixtures. Wooten, et al. (29) have applied the combined techniques to the analysis of solvent refined coal.

Proton resonance, which has already been demonstrated to be an invaluable means of fuel analysis, suffers from the single disadvantage of being blind to carbons which have no hydrogens attached. This weakness is mitigated by the fact that the number of these carbons can often be estimated from data for protons on adjacent carbons. Additional work remains to be done on ^{13}C NMR structural correlation for hydrocarbon fuels, and attention is

required on the quantitative aspects of the ^{13}C Fourier transform technique. However, this analytical approach may ultimately become the choice method in terms of accuracy and economy, for characterizing fuel compositions.

3. GAS CHROMATOGRAPHY (GC)

Methods for gas chromatographic hydrocarbon type analysis generally fall into one of two categories. Compound class separations are often attained before the materials enter the chromatographic column by using selective absorbants or reactants. The other common approach employs a column containing a strongly polar liquid phase having very little affinity for saturated and olefinic hydrocarbons, and yet a pronounced selectivity for aromatics. Frequently the two approaches are combined for an effective separation.

Martin (30), who developed the first hydrocarbon type analysis for gasoline using a highly polar stationary phase, investigated a large number of liquid phases before choosing β,β'-thiodipropionitrile. Saturates were eluted from this column in one large peak before the lowest boiling aromatic, benzene, appeared. Olefins were distinguished from paraffins by absorbing the former in mercuric perchlorate-perchloric acid, which allowed the saturates to pass. By use of a liquid nitrogen trap and a backflush technique, the olefin-free paraffins were passed through the thermal conductivity detector a second time. Saturates and aromatics were determined directly from peak areas; olefins were determined by the difference between the areas for saturates plus olefins and for saturates alone.

Albert (31) modified Martin's method by the addition of a Type 5A molecular sieve column and by using N,N'-bis(2-cyanoethyl) formamide (CEF) as the selective liquid phase, enabling him to

determine aromatics, olefins, isoparaffins, cycloparaffins, and n-paraffins in a single injection of a gasoline sample.

The use of a mercuric perchlorate absorber for olefins was later (32) recognized as a serious source of error, with as much as 25% of some C_9-C_{11} saturates being lost thereby. Souloges (33) controlled the acid concentration of the absorber by humidifying the carrier gas and found that, by this means, loss of saturated hydrocarbons was prevented.

Use of 2,4,6-trinitrophenetole as a stationary phase (34) caused benzene in gasoline samples to emerge from the column between n-undecane and dodecane. The total aromatic content of narrow petroleum fractions boiling up to 480°F have been determined using a column of tetracyanoethyl ether (35).

A number of other aromatic selective liquid phases have subsequently been used. The separation mechanism of these materials is the rejection of aliphatics rather than retention of aromatics. The degree of success experienced in using a material of this type is measured by the ease and speed with which aliphatics are rejected. Other highly polar columns and typical benzene/decane retention times are presented in Table 102. A limitation of many columns of this type lies in their upper temperature limit of 175-200°C. Most of the analytical methods developed using these columns are for the analysis of gasoline or light naphthas. The instability of these materials at reasonably elevated temperatures presents an obstacle, though not an insurmountable one, to their use for analysis of higher boiling fuels.

One application of polar liquid phases which has not been fully explored is for coating capillary columns. Wall coated open tubular columns frequently are more effective at higher temperatures than a packed column with the same stationary phase.

TABLE 102. TYPICAL COLUMNS FOR AROMATIC COMPOUND SELECTIVITY

Liquid Phase	Retention Times (min) Decane/Benzene	Length (ft)[a]	Wt. Percent[a]	Upper Temp. Limit (°C)[c]
Diethyleneglycol succinate (DEGS)	2.3/2.9	8	20	200
Polyethylene glycol-400 (PEG)	6.8/7.6	10	-	150
Tetracyanoethylated pentaerythritol (TCEPE)	2.6/3.0	15/16	10/15	175
1,2,3 Tris(2-cyano-ethoxy)propane (TCEP)	10.2/15.2	20	20	175
Carbowax 1540	-	300[b]	8[b]	175

[a]ASTM Method D2267, Part 24, 1975 Annual Book of ASTM Standards

[b]Universal Oil Products Method 744-77

[c]Supelco Inc., Bellefonte, Penn. 16823, Catalog 11

That is, higher molecular weight materials, which remain on a packed column at a given temperature, are frequently eluted from a capillary column at the same temperature.

An illustration of this effect is given in a method (37) in which a 91.4-meter capillary coated with Carbowax 1540 is used. This liquid phase allows the rapid passage (before benzene) of all aliphatic components in gasoline. With the column temperature maintained at 95°C for maximum resolution, aromatic components up to 1,2,3,4-tetramethylbenzene, boiling at 205°C, are eluted. Operated at its maximum temperature of 175°C this column should be useful for substantially higher boiling fuels.

Capillary columns coated with highly polar liquid phases offer promise as excellent tools for aromatic hydrocarbon analysis. A preliminary distillation of the fuel into narrower-range fractions may be necessary to ensure that the highest-boiling paraffin has cleared the column before the first aromatic constituent appears.

4. LIQUID CHROMATOGRAPHIC METHODS

One of the most commonly used methods for the determination of hydrocarbon types is described in ASTM D1319 (37) as the FIA (fluorescent indicator analysis) method. The technique consists of a displacement chromatographic procedure which, while rapid, gives an approximate answer and is subject to a variety of manual and visual human errors. Silica gel, which is the adsorbent used in the FIA method, has been used in a variety of other chromatographic procedures for aromatic/aliphatic separations in hydrocarbon analysis (38-40). In early work the separations were commonly followed by rechromatographing the aromatic fraction through alumina (41, 42). In both steps, elution chromatographic techniques with solvents of differing

polarity were employed. L. R. Snyder later proposed the use of partially deactivated silica gel (43-45) and γ-alumina modified with water, to obtain adsorption isotherm linearity.

In more recent work (46) three principles were utilized in low and medium pressure liquid/solid elution chromatography for analysis of petroleum distillates. In this work, either alumina or silica gel, modified with 2-15% water, was used to obtain a separation of saturated hydrocarbons, monocyclic aromatic hydrocarbons and bicyclic aromatic hydrocarbons. It was shown that the water-modified adsorbents gave essentially no irreversible selective sorption of hydrocarbons in the three classes studied. Moreover the technique showed a high selectivity for one hydrocarbon class practically independent of the length of the alkyl substituents. Thus for substituted aromatic hydrocarbons, the interaction of even long chain alkyl groups with the adsorbent surface was insignificant.

Stevenson (47) employed a liquid/liquid high pressure chromatographic approach, using a column of silica impregnated with 30% Carbowax 600, for the analysis of these same hydrocarbon classes. While somewhat more rapid than the liquid/solid technique discussed above, the method was not nearly as independent of the number and size of aromatic ring substituents. However, sufficient separation of aromatics and paraffins is usually obtained. For paraffins, the range of retention times were remarkably similar, probably due to the low affinity of the liquid phase for paraffins.

Hirsch, et al. (48) developed a liquid/solid chromatographic procedure to separate high-boiling petroleum fractions into four relatively distinct compound types, namely, saturates, monoaromatics, diaromatics and polyaromatic/polar compounds. For this purpose a dual packed silica gel alumina column was used.

Prior to adsorption, anion and cation resins were used to remove acid and basic constituents and ferric chloride was used to remove neutral nitrogen compounds. Use of the dual column packing lessened the need for partial deactivation of the adsorbents, thereby retaining the original adsorptive capacity of the adsorbent material. Sufficient sample volume was thus possible so that the various fractions could be quantified by solvent stripping and weighing. Five solvents ranging in polarity from pentane to methanol were used for elution of the four fractions.

Suatoni et al. (49) developed a high performance liquid chromatographic (HPLC) method for the analysis of hydrocarbon type groups in gasolines and higher distillation range jet fuel. These workers used a low polarity perfluorocarbon mobile phase and a column packed with a small particle silica (μ-Porasil) to obtain relative amounts of saturates, aromatics and olefins. The refractive indices of mono aromatics are fairly constant (±2%) over the range of C_6-C_{12} benzenes. A calibration for aromatics thus provided a reliable measure of the volume percent aromatics using the refractive index (RI) detector. A wide variation in refractive index with structure and molecular weight is observed for paraffins and clefins, however these materials were measured by difference.

Suatoni and Swab (50) developed a HPLC method which is suitable for the analysis of practically all hydrocarbon fractions from gasolines to total crude oils. Saturates, aromatics, polar components and hexane-insolubles can be determined. The latter groups are preliminarily removed by clay treatment and filtration, respectively. The procedure utilizes a μ-Porasil column and dried reagent-grade hexane as the mobile phase.

A problem common to most HPLC methods involves the procedure used for quantification. Unlike the flame ionization detector used in gas chromatography, there is no HPLC detector which responds to hydrocarbons on an approximate weight or volume percent basis. The response of the U.V. absorption detector varies substantially with the type of aromatic compound and its degree of substitution. The RI detector response similarly varies with the structure of paraffins. Calibrations based on compounds expected to be present have been made, or in some cases actual samples similar to those being analyzed are fractionated for use in calibration. Fodor and Newman (51) in developing a calibration procedure for use in HPLC analysis of middle-distillate fuels, found that the working relation between model compounds and actual fuels was very poor. As an alternate approach these investigators decided to compare the response of preparatively cut saturated fuel fractions, in the hope that only one response factor for all fuels within the same boiling range would be required. However unacceptable errors resulted in this method of calibration and these workers ultimately decided that, for best results, the saturate fraction of each fuel should be cut by preparative HPLC and response from this fraction compared to that of the neat fuel.

Despite the difficulty in obtaining suitable calibration for fuels in some boiling ranges, the liquid chromatographic approach offers promise as a rapid means for hydrocarbon type analysis. The technique is especially useful when a detailed analysis, including a number of different hydrocarbon classes, is not required.

5. EXAMINATION OF SPECIFIC NMR APPROACHES TO HYDROCARBON TYPE ANALYSIS

Mass spectrometry has perhaps been the technique most fully exploited for hydrocarbon type analysis to this time. Both gas

and liquid gas chromatographic methods have also been in common use for samples of specific types and boiling ranges. With the development of new instrumentation and column materials, additional useful methodology continues to be developed. Nuclear magnetic resonance, on the other hand, is just finding acceptance as a hydrocarbon-type analysis technique. Specific NMR approaches, as they might apply to jet turbine fuels, have been examined.

Proton Resonance

Myers, et al. (25) have developed a proton resonance method for the analysis of gasolines which incorporates a correction for the carbon atoms that cannot be detected because of the absence of attached protons. To establish this correction, information on typical fuel compositions was used. By making modifications in the Myers method, it was believed that the method could be made suitable for a variety of fuels without having the assurance that the fuels fit a typical composition. The feasibility of such a modification was investigated. The average carbon number of a fuel can be estimated from a gas chromatographic simulated distillation and is equal to a carbon number corresponding to the 50% point. This value represents the average carbon number of the normal paraffin content (Cp). A reasonable estimate of the carbon number of the aromatic portion (Ca) is equal to Cp-1 (52). Instead of attempting to predict the number of carbons in alkyl chains attached to mono-aromatic rings, that value can be calculated as Ca-6. The only carbon atom in the aromatic ring having no protons are those to which an alkyl chain is attached. These "hidden" carbon atoms can be counted and are equivalent to the number of alpha carbons, a number readily measured. Thus all alkylbenzene carbon atoms are counted. In order to produce results in liquid volume percent, Myers incorporates a factor which is equivalent to the ratio of the density of the aromatic fraction to the paraffin fraction. This ratio would not be expected to change greatly for the more extended boiling range of turbine fuels.

Proton NMR spectra were recorded for several jet fuels which had been previously analyzed by mass spectrometry. The volume percent of the aromatic and saturated fractions were calculated using a method similar to that of Myers et al. (25) but having the above modifications. Required spectral information and the equations used are presented in Table 103. A typical NMR spectrum is presented in Figure 62. The values for aromatic and paraffin content calculated using the equations in Table 103 are presented in Table 104 and are compared to the values obtained by mass spectrometry. The agreement between the two methods is sufficiently good to suggest that such an NMR approach can provide a useful and rapid means of establishing a fuel's aromatic content. Further refinement of the equations are doubtlessly possible, to make them more applicable to jet fuels.

Carbon-13 Resonance

Because of the form in which mass spectral and chromatographic hydrocarbon type data are obtained, investigators almost universally have treated NMR analyses in various ways to make them comparable to results obtained by these standard hydrocarbon evaluation techniques. Chromatographic techniques generally categorize any compound containing an aromatic ring as aromatic and any compound containing a double bond as olefinic. A compound such as butylbenzene, however, contains 40% aliphatic carbon and 60% aromatic carbon as determined by NMR. Some compounds such as higher alkyl benzenes, substituted tetralins, etc. may have a higher percent of aliphatic and naphthenic carbon than aromatic carbon, though they are categorized as aromatic. The question arises as to how the composition of a petroleum fuel should be generally described to best correlate with physical and chemical properties.

Carbon-13 NMR is essentially a technique in which carbon atoms are sorted according to their structural position.

TABLE 103. USE OF PROTON RESONANCE DATA FOR CALCULATION OF AROMATIC AND PARAFFINIC CONTENTS(a)

Assignment	Shift, ppm	Designation
Aromatic Ring	6.6 - 8.0	A
Olefin	4.5 - 6.0	B
α-Methyl	2.0 - 3.0	C
Methine	1.5 - 2.0	D
Methylene	1.0 - 1.5	E
Methyl	0.6 - 1.0	F
Ave. Carbon Number of Aromatic Fractions	Determined by gas chromatography	Ca#

$$\% \text{ Paraffins} = \frac{[(D + \frac{E}{2} + \frac{F}{3}) - (A + \frac{C}{3})(1 - \frac{6}{Ca\#})]1.02 \times 10^2}{[(D + \frac{E}{2} + \frac{F}{3}) - (A + \frac{C}{3})(1 - \frac{6}{Ca\#})]1.02 + (A + \frac{C}{3})0.7572\ \frac{Ca\#}{6}}$$

$$\% \text{ Aromatics} = \frac{(A + \frac{C}{3})0.7572\ \frac{Ca\#}{6} \times 10^2}{[(D + \frac{E}{2} + \frac{F}{3}) - (A + \frac{C}{3})(1 - \frac{6}{Ca\#})]1.02 + (A + \frac{C}{3})0.7572\ \frac{Ca\#}{6}}$$

(a) Modification of method by Myers, Stollsteimer and Wims (25).

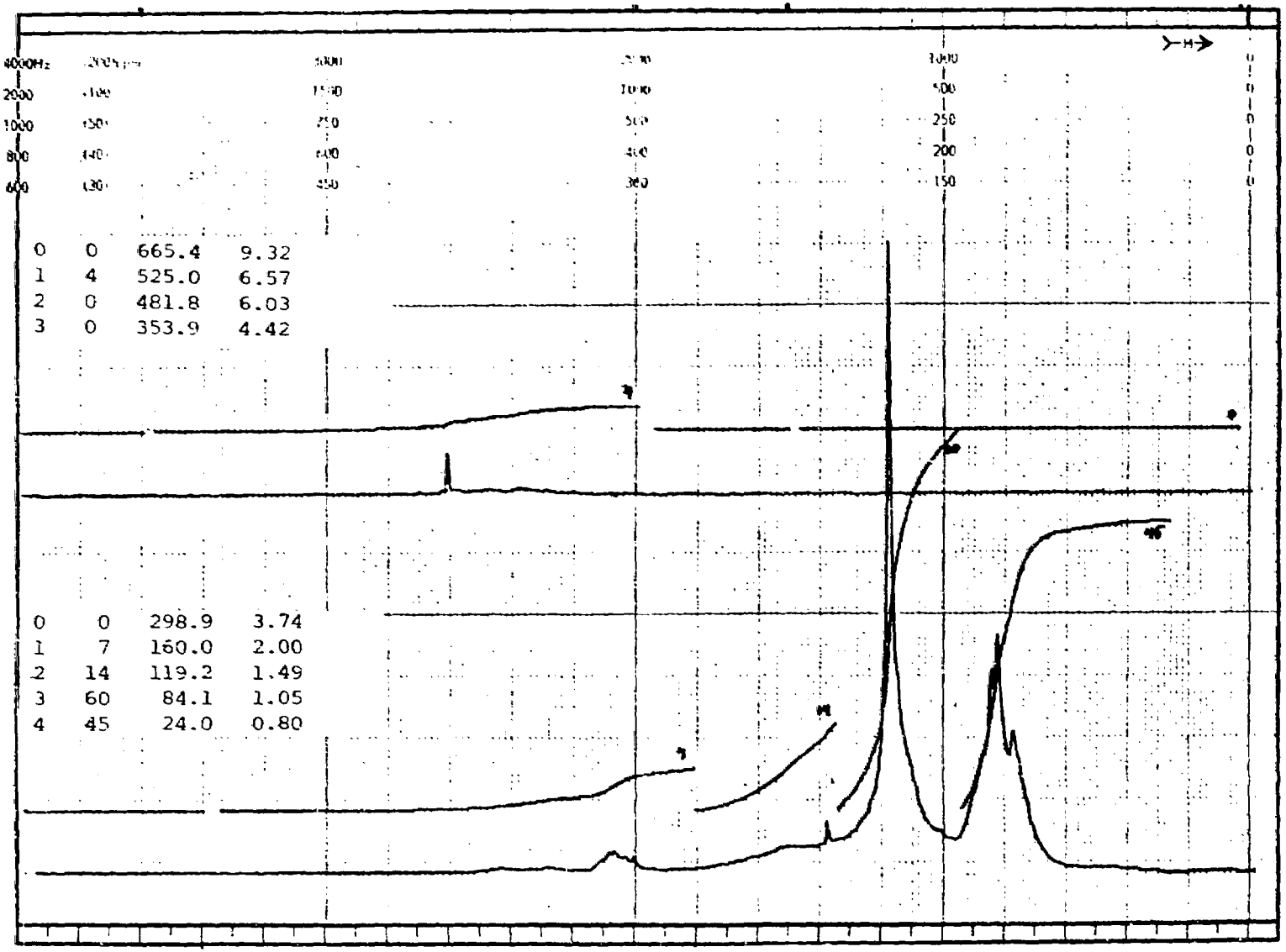


Figure 62. Proton resonance spectrum of JP-8 fuel showing integration of characteristic regions for hydrocarbon type analyses.

TABLE 104. COMPARISON OF MASS SPECTRAL AND NMR CALCULATIONS

Fuel	Mass Spectrometry	Proton Resonance NMR
AFFB-16-73, JP-4	8.9% aromatic[a] 91.1% paraffin	8.0% aromatic 92.0% paraffin
Syncrude JP-4	13.0% aromatic[a] 87.0% paraffin	12.5% aromatic 87.5% paraffin
Conventional JP-4	9.4% aromatic[a] 90.6% paraffin	9.3% aromatic 90.7% paraffin
Shale Oil Jet A	21.4% aromatic[a] 78.6% paraffin	19.3% aromatic 80.7% paraffin
Baseline JP-8	13.5% aromatic[b] 86.5% paraffin	13.7% aromatic 86.3% paraffin

[a] Complete analysis presented in Technical Report AFAPL-TR-76-26 (March 1976)

[b] Complete analysis presented in Section IV of this report

The technique was investigated for use on a specimen of JP-8 which had been characterized in detail by a variety of methods as presented in Section IV of this report. Values for a number of operational parameters were varied in order to evaluate their effect on data accumulated by the ^{13}C Fourier transform NMR technique. The investigation was conducted on a Varian CFT-20 FT NMR spectrometer at 20 MHZ. A varian 620 L data acquisition and reduction system is a part of that instrument. Various instrument conditions were evaluated and the recommended conditions were used. Use of chromium acetylacetonate (CrAcAc) or similar relaxation agent is essential.

Chemical shifts in the 10-50 ppm range relative to tetramethyl silane were used as a measure of saturated carbons, and the 120-150 ppm range was used for aromatic carbons. A calculation of the atom or weight percent of aromatic and saturated carbon is performed by integration of bands in these regions as shown in

Figure 63. For the JP-8, the aromatic area was 14 and the saturated area was 158 to yield an aromatic carbon value of 8.1%.

The mass spectral hydrocarbon type data presented in Section IV can be re-computed to determine weight percent aromatic carbon as shown below.

Aromatic Constituents	Analyzed Weight Percent	Average Compcund	% Aromatic Carbon	% Saturated Carbon
Alkybenzene	7.5	$C_{11}H_{16}$	3.65	3.04
Indans and Tetralins	3.8	$C_{11}H_{14}$	1.87	1.56
Indenes	0.5	$C_{11}H_{12}$	0.35	0.29
Naphthalene	1.5	$C_{11}H_{10}$	1.15	0.11
			7.02	5.00

Saturated Constituents

	Weight %	Average Compound	% Saturated Carbon
Paraffins	41.8	$C_{12}H_{26}$	35.8
Cycloparaffins	37.5	$C_{12}H_{24}$	31.8
Dicycloparaffins	6.1	$C_{12}H_{22}$	5.3
Tricycloparaffin	1.1	$C_{12}H_{20}$	0.97
			73.9

Percent Aromatic Carbon is thus = $\frac{7.02 \times 100}{7.02 + 73.9 + 5.0}$ = 8.2%

The excellent agreement of this value with the one determined by ^{13}C FT NMR indicates the potential utility of the NMR method. Further work would, of course, be required to validate this approach for a wide range of fuels. The mass spectral method is rather time consuming and was preceded by a separation into aromatic and saturated fractions. The NMR method is quite rapid and would represent a great savings in time if proven suitable. The most important factor in favor of the ^{13}C NMR approach is that the values for aromatic and saturated carbon may be more meaningful in terms of the combustion properties of fuels than any other data obtainable.

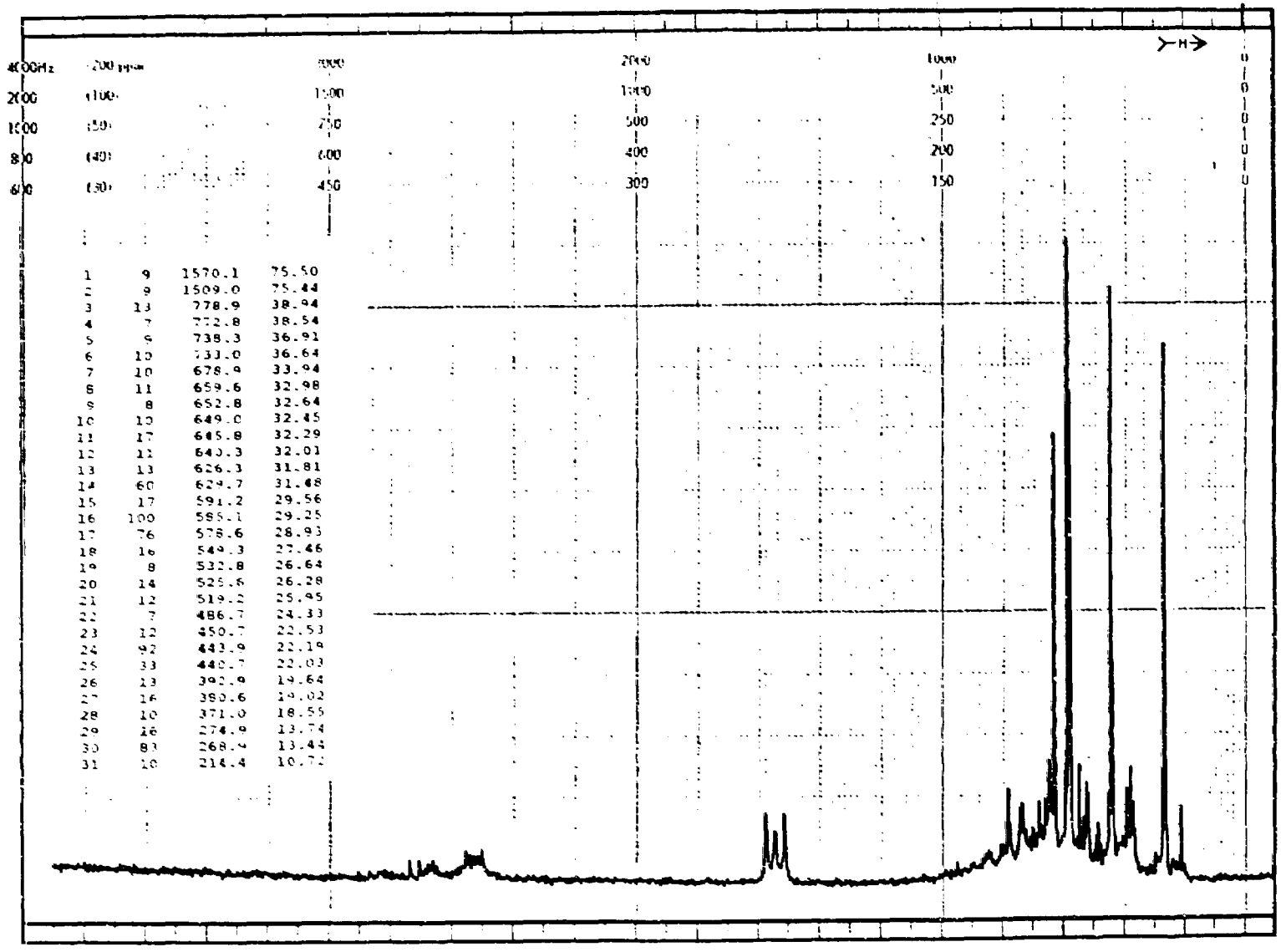


Figure 63. Nuclear magnetic resonance spectrum of JP-8 by ^{13}C FT technique.

Consider for example the effect of aromatic composition on smoke point (ASTM D-1322). Hunt (53) has shown, by data on a large number of pure compounds, that smoke point varied according to the general trend:

paraffins > naphthenes > aromatic

with branching, or branched substituents, effectively decreasing the smoke point. In testing binary mixtures of 20% aromatic compound in n-dodecane, Hunt showed that smoke point tended to increase as the size of the alkyl substituent increased within an homologous series. He further demonstrated that mixtures containing naphthalene had lower smoke points than blends of alkylbenzenes at the same concentration. Typical values are presented in Table 105.

TABLE 105. SMOKE POINT VALUES FOR 20% BLENDS OF INDIVIDUAL AROMATICS IN DODECANE

Aromatic constituent	Percent aromatic carbon in aromatic constituent	Smoke point of blend (Ref 53)
n-alkylbenzenes		
ethylbenzene	75	64
propylbenzene	66.6	78
butylbenzene	60	80
sec-alkylbenzenes		
sec-propylbenzene	66.6	71
sec-butylbenzene	60	76
sec-amylbenzene	54.5	81
naphthalene	100	42

These data indicate that smoke point correlates better with the percent aromatic carbon than it does with the total aromatic content as defined by chromatographic procedures. Factors such as branching influence smoke point, but all types of monoalkylbenzenes show increased blended smoke points for increased alkyl chain size.

The hydrogen content of a fuel has been demonstrated to be an excellent measure of its combustion performance (54). Physical properties such as a luminometer number, heat of combustion and smoke volatility index, correlate well with hydrogen content (55). The hydrogen content of a fuel, however, is governed to a great extent by the amount and kinds of aromatics in its composition. This fact is recognized in fuel specifications by establishing a maximum allowable level of naphthalenes independent of the maximum aromatic content.

The carbon counting nature of the ^{13}C NMR technique, then, provides data for fuels which can be directly correlated with combustion behavior. Computations to determine compositions in terms of the actual compounds present are not necessary and only require error-producing assumptions.

Conclusions

Proton resonance, which has already been demonstrated to be a valuable means of fuels analysis, suffers from the single disadvantage of being blind to carbons which have no hydrogens attached. This weakness is mitigated by the fact that the number of these carbons can often be estimated from data for protons on adjacent carbons.

Much additional work remains to be done on ^{13}C NMR structural correlation for hydrocarbon fuels, and attention is required on the quantitative aspects of the ^{13}C Fourier transform technique. However, this analytical approach may become the choice method in terms of accuracy and economy, for characterizing fuel compositions.

SECTION VI

GENERAL SUPPORT ANALYSES

A number of analyses were conducted in a general support function to characterize fuels of various origins. The principal task in this category was designated 6.1 support in which JP-4, JP-8, Jet A, JP-7, and modified and shale derived fuels were rather completely characterized. Data for simulated distillation by gas chromatography (ASTM D2887) are presented in Table 106. Hydrocarbon type analyses by mass spectrometry are presented in Table 107 and heat of combustion values are given in Table 108. Nitrogen and sulfur content are presented in Table 109.

In support of another Air Force program, dielectric constant values were measured for various JP-8 fuels. Dielectric constants as a function of temperature were measured at 400 Hz for four specimens of JP-8 fuel. Samples were:

1. JP-8, clay treated and filtered with 45μ millipore filter.
2. JP-8, clay treated and filtered, 0.1% FSll added.
3. JP-8, clay treated and filtered, Hitec 515 added (10 lb/1000 bbl).
4. JP-8, clay treated and filtered, Hitec 515 (10 lb/1000 bbl) and 0.1% FSll added.

A General Radio 1615A capacitance bridge and guard circut were used for the measurements. The bridge signal generator was a General Radio 1311A Audio Oscillator and the bridge detector was a Type 1232A tuned amplifier and null detector.

Capacitance measurements were taken at each of four temperatures for the empty three-terminal sample cell and then again after filling the cell with the sample. An eight-hour period was

TABLE 106. SIMULATED DISTILLATION BY GAS CHROMATOGRAPHY (ASTM D2887)

	VI/NR-77-01 Modified JP-4		VI/NR-77-03 JP-8		VI/NR-77-04 Modified JP-8		VI/NR-77-05 Modified JP-8		VI/NR-77-06 JP-7		VI/NR-77-07 JP-7	
	Boiling Point											
Percent Recovered	°C	°F	°C	°F	°C	°F	°C	°F	°C	°F	°C	°F
0.5 (Initial Boiling Point)	33	91.4	111	232	120	248	115	239	157	315	156	314
5	87	189	158	317	163	326	160	320	179	354	180	356
10	99	211	170	338	175	348	171	340	192	378	191	376
20	121	250	183	361	190	375	186	366	202	396	204	398
30	150	302	197	387	203	397	198	388	212	414	214	416
40	180	356	207	405	214	417	213	415	219	426	223	433
50	203	397	219	426	227	441	224	434	228	442	230	446
60	218	424	230	446	234	453	236	457	235	455	238	460
70	230	447	241	465	243	469	252	486	243	469	246	474
80	237	459	256	493	256	493	268	514	253	487	255	491
90	255	491	273	523	274	525	291	556	261	501	266	511
95	270	518	286	547	287	548	306	582	268	514	272	522
99.5 (End Point)	303	577	310	590	318	604	334	632	280	536	288	550

	VI/NR-77-08 Unidentified		VI/NR-77-09 Jet A		VI/NR-77-10 JP-7		VI/NR-77-11 Shale Oil JP-4		VI/NR-77-12 Shale Oil Jet A		VI/NR-77-13 JP-4	
	Boiling Point											
Percent Recovered	°C	°F	°C	°F	°C	°F	°C	°F	°C	°F	°C	°F
0.5 (Initial Boiling Point)	108	226	99	210	149	308	10	50	70	157	34	93
5	129	265	144	291	173	343	89	192	120	248	62	143
10	136	277	165	329	185	365	98	208	147	297	69	157
20	154	309	186	366	200	391	112	237	174	344	86	188
30	164	326	198	388	211	411	126	258	189	372	96	206
40	176	349	208	406	218	424	135	275	200	392	104	219
50	188	370	216	421	222	431	150	302	217	422	123	253
60	198	388	223	433	232	450	161	321	226	439	166	331
70	210	411	232	449	238	460	175	345	237	459	196	385
80	220	428	239	461	246	475	185	365	253	487	217	423
90	236	458	254	489	254	489	198	389	270	518	237	460
95	240	464	264	507	260	500	215	419	281	538	253	487
99.5 (End Point)	267	513	293	559	276	529	241	466	311	591	283	541

	VI/NR-77-14 JP-4		VI/NR-77-15 JP-4		VI/NR-77-16 JP-4		VI/NR-77-17 JP-4		VI/NR-77-18 JP-4		VI/NR-77-19 JP-4	
	Boiling Point											
Percent Recovered	°C	°F	°C	°F	°C	°F	°C	°F	°C	°F	°C	°F
0.5 (Initial Boiling Point)	32	89.6	27	81.5	54	129	5	41.0	31	88.7	27	81.5
5	63	145	69	156	68	154	76	170	75	167	74	166
10	90	194	83	182	70	159	100	212	94	202	90	195
20	119	247	99	210	89	193	127	261	105	222	103	218
30	141	287	108	227	100	212	149	301	122	252	120	248
40	157	316	120	249	117	243	162	324	131	268	134	274
50	172	342	131	268	134	273	171	341	149	300	150	302
60	186	368	147	297	151	305	179	354	171	340	166	332
70	200	393	162	324	171	341	188	371	191	377	183	362
80	217	424	181	359	195	383	197	387	213	416	204	400
90	238	460	219	427	219	427	204	399	237	460	225	437
95	255	491	246	475	238	460	215	420	255	491	241	467
99.5 (End Point)	293	559	285	545	272	522	241	466	282	540	279	535

TABLE 107. HYDROCARBON TYPE DISTRIBUTION

Compound Type	Volume Percent								
	VI/NR-77-01 Modified JP-4	VI/NR-77-03 JP-8	VI/NR-77-04 Modified JP-8	VI/NR-77-05 Modified JP-8	VI/NR-77-06 JP-7	VI/NR-77-07 JP-7	VI/NR-77-08 Unidentified	VI/NR-77-09 Jet A	VI/NR-77-10 JP-7
Paraffins	39.2	45.1	34.5	46.1	56.3	56.0	54.1	39.4	50.1
Monocycloparaffins	22.0	39.5	30.3	39.3	38.7	39.1	38.5	41.4	43.7
Dicycloparaffins	None detected	2.4	1.7	2.1	0.9	0.8	0.4	1.9	2.9
Alkylbenzenes	12.2	7.8	10.6	7.5	3.1	3.1	4.8	9.0	2.6
Indans & Tetralins	4.6	3.3	4.9	3.2	0.7	0.7	1.2	5.7	0.5
Naphthalenes	22.0	1.9	18.0	1.8	0.3	0.3	1.0	2.6	0.2

Compound Type	Volume Percent								
	VI/NR-77-11 Shale Oil JP-4	VI/NR-77-12 Shale Oil Jet A	VI/NR-77-13 JP-4	VI/NR-77-14 JP-4	VI/NR-77-15 JP-4	VI/NR-77-16 JP-4	VI/NR-77-17 JP-4	VI/NR-77-18 JP-4	VI/NR-77-19 JP-4
Paraffins	66.6	57.4	54.0	57.2	52.3	61.9	47.7	64.0	26.6
Monocycloparaffins	20.0	23.3	32.9	32.4	36.0	21.7	30.2	22.1	49.6
Dicycloparaffins	2.0	None detected	3.8	None detected	3.7	2.1	7.0	5.2	12.9
Alkylbenzenes	10.0	9.4	7.1	9.1	7.2	13.7	13.8	7.0	8.0
Indans & Tetralins	1.4	7.7	1.3	0.7	0.6	0.4	1.0	1.1	2.1
Naphthalenes	None detected	2.2	0.9	0.6	0.2	0.2	0.3	0.6	0.8
Average Carbon No.	8.8		8.9	10.0	8.9	8.6	9.4	9.3	9.5

TABLE 108. HEAT OF COMBUSTION DATA FOR 6.1 SUPPORT FUELS

	Heat of Combustion	
	Gross, Btu/lb	Net, Btu/lb
VI/NR-77-01 Modified JP-4	19,317	
	19,296	
	Average 19,307	18,194
VI/NR-77-03 JP-8	19,804	
	19,815	
	Average 19,810	18,541
VI/NR-77-04 Modified JP-8	19,323	
	19,320	
	Average 19,322	18,188
VI/NR-77-05 Modified JP-8	19,846	
	19,822	
	Average 19,834	18,560
VI/NR-77-06 JP-7	20,067	
	20,044	
	Average 20,056	18,721
VI/NR-77-07 JP-7	20,063	
	20,069	
	Average 20,066	18,735
VI/NR-77-08 Unidentified	20,023	
	19,984	
	Average 20,004	18,681
VI/NR-77-09 Jet A	19,690	
	19,741	
	Average 19,716	18,462
VI/NR-77-10 JP-7	20,050	
	20,080	
	Average 20,065	18,771
VI/NR-77-11 Shale Oil JP-4	20,084	
	20,067	
	Average 20,076	18,754
VI/NR-77-12 Shale Oil Jet A	19,736	
	19,735	
	Average 19,736	18,472
VI/NR-77-13 JP-4	20,032	
	20,054	
	Average 20,043	18,734
VI/NR-77-14 JP-4	20,086	
	20,043	
	Average 20,065	18,748
VI/NR-77-15 JP-4	20,114	
	20,078	
	Average 20,096	18,771
VI/NR-77-16 JP-4	20,028	
	20,016	
	Average 20,022	18,713
VI/NR-77-17 JP-4	19,912	
	19,949	
	Average 19,931	18,648
VI/NR-77-18 JP-4	20,139	
	20,125	
	Average 20,132	18,799
VI/NR-77-19 JP-4	19,848	
	19,864	
	Average 19,856	18,592

TABLE 109. TRACE ELEMENT ANALYSIS

	Nitrogen	Sulfur, ppm by wt.
VI/NR-77-01 Modified JP-4	Trace, <25 ppm	245
VI/NR-77-03 JP-8	Trace, <25 ppm	566
VI/NR-77-04 Modified JP-8	Trace, <25 ppm	400
VI/NR-77-05 Modified JP-8	Trace, <25 ppm	526
VI/NR-77-06 JP-7	Trace, <25 ppm	4
VI/NR-77-07 JP-7	None detected	3
VI/NR-77-08 Unidentified	None detected	740
VI/NR-77-09 Jet A	None detected	500
VI/NR-77-10 JP-7	None detected	<1
VI/NR-77-11 Shale Oil JP-4	121 ppm, 122 ppm	21
VI/NR-77-12 Shale Oil Jet A	683 ppm	35
VI/NR-77-13 JP-4	None detected	1,089
VI/NR-77-14 JP-4	Trace, <25 ppm	73
VI/NR-77-15 JP-4	None detected	94
VI/NR-77-16 JP-4	None detected	456
VI/NR-77-17 JP-4	None detected	155
VI/NR-77-18 JP-4	None detected	183
VI/NR-77-19 JP-4	None detected	851

allowed for temperature equilibration of the empty cell in each case and for the cell containing fuel at the subambient temperature. Equilibration of 74°F and 100°F was at least four hours. Constant temperature baths were controlled within ± 0.25°F. The sample cell was disassembled, cleaned and oven dried after each measurement to prevent cross contamination of the fuels.

Parts of the sample cell which were exposed above the coolant in the low temperature baths were wrapped with glass wool for insulation and sealed with polyethylene sheeting to prevent wetting due to condensation of atmospheric moisture.

Dielectric constant values are given in Table 110.

TABLE 110. DIELECTRIC CONSTANTS OF JP-8 SPECIMENS

	Temperature (°F)			
	-65°	0°	74°	100°
Sample 1	2.2082	2.1603	2.1038	2.0876
Sample 2	2.2126	2.1634	2.1050	2.0865
Sample 3	2.2051	2.1625	2.1042	2.0871
Sample 4	2.2096	2.1696	2.1077	2.0895

SECTION VI

CONCLUSIONS

1. Physical measurements of a wide variety of fuel properties on JP-9 indicate that the numerical value of the properties do not vary significantly for various batches of RJ-5.

2. Accurate and precise analysis can be performed to determine the composition of JP-9 fuels using a gas chromatographic method in which response factors are determined for JP-9 components relative to methylcyclohexane (MCH). By using RJ-5 and mono-and polyisomeric THD from six different lots, it was found that average response factors could be determined which were valid for use in the analysis of JP-9 containing RJ-5 and THD from any one of the individual lots. It can be concluded that this average response factor would be valid for the analysis of JP-9 regardless of the source of its components.

3. Tyndall light scattering is a sensitive and rapid method for measuring suspended matter in liquids. Studies show that the technique may be useful as a means of detecting additive incompatibility when it is manifested by the formation of a fine suspension.

4. A candidate non-hazardous calibrating fluid, composed of Freon® TF and a low-volatility hydrocarbon oil, was shown to have desirable characteristic such as good seal compatibility. However, the high evaporative loss, resulting in a composition change for the blend, will limit its usefulness as a calibrating fluid.

5. In surveying methods of hydrocarbon type analysis, NMR was found to have great potential because the aromaticity measured

by that approach can be more directly related to fuel combustion behavior than can data from other analytical techniques. Moreover, the analysis is rapid and applicable to all fuel types. A great potential exists in a combined proton and carbon-thirteen (^{13}C) approach.

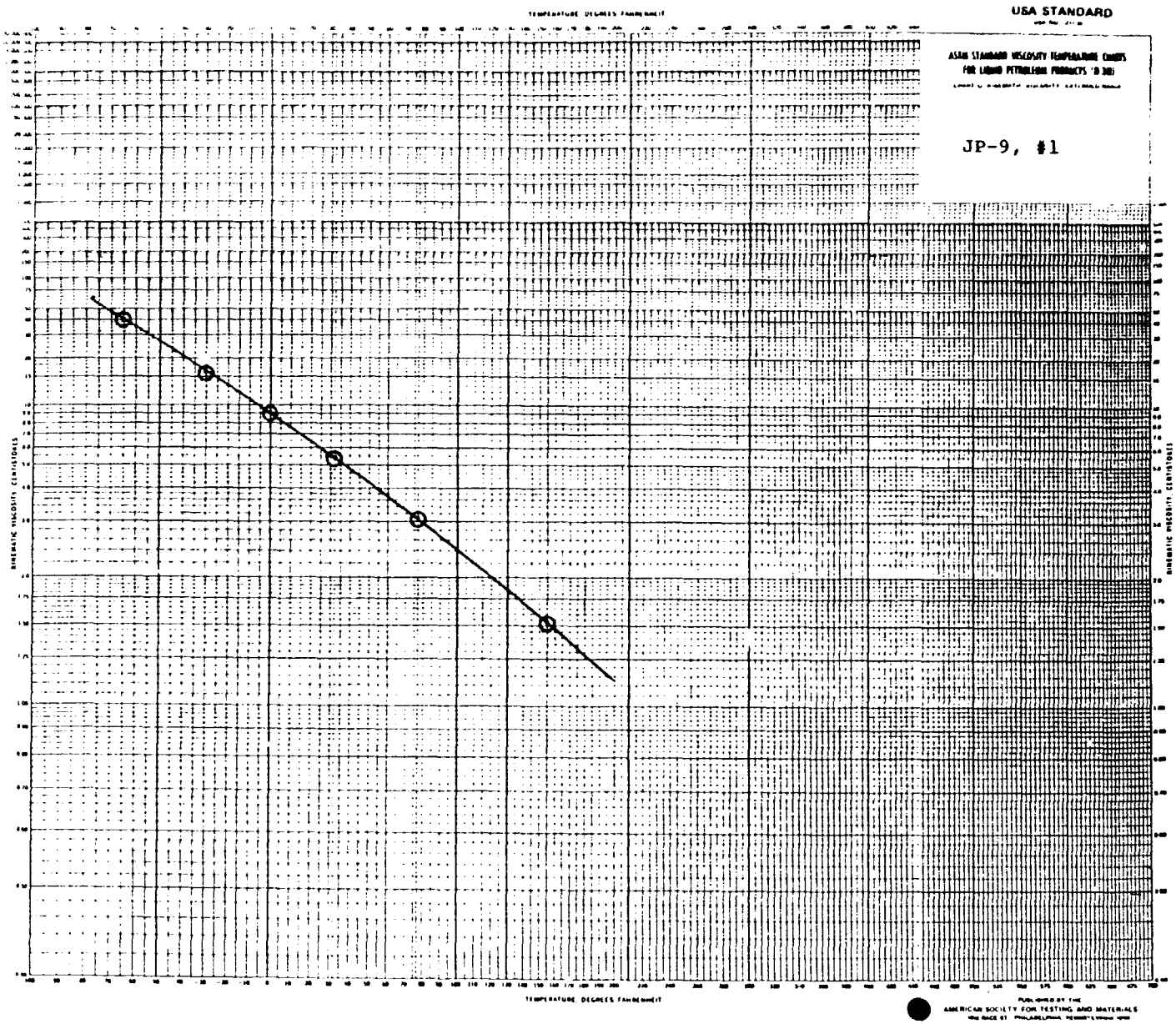
A major portion of the work under the program was devoted to the generation of physical and chemical property data for use in various Air Force programs. No conclusions, other than the fundamental information produced, are warranted from this phase of the effort. Analyses in conjunction with Air Force in-house and contractual programs have been conducted and conclusions resulting from these analyses will be obtained later at the completion of those programs.

Other parts of the work under this program have been varied and of a problem-solving nature. A number of separate and unrelated investigations were conducted. For better clarity and continuity, conclusions for those studies are presented along with discussion of the work in the various Sections.

APPENDIX A

ASTM VISCOSITY CHARTS

Fuels Discussed in Subsections 1 and 4 of Section I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KINEMATIC VISCOSITY CENTISTOKES
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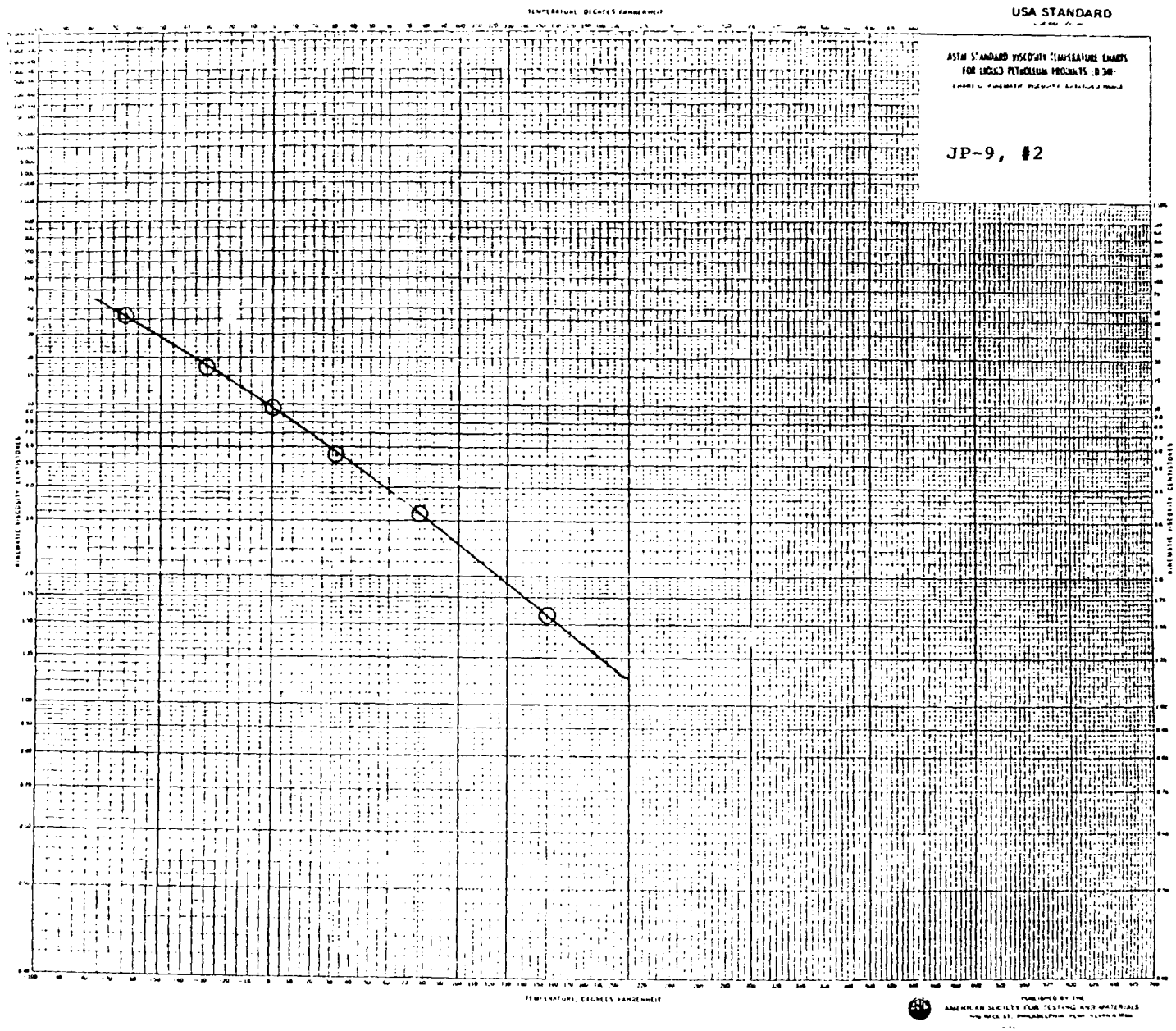
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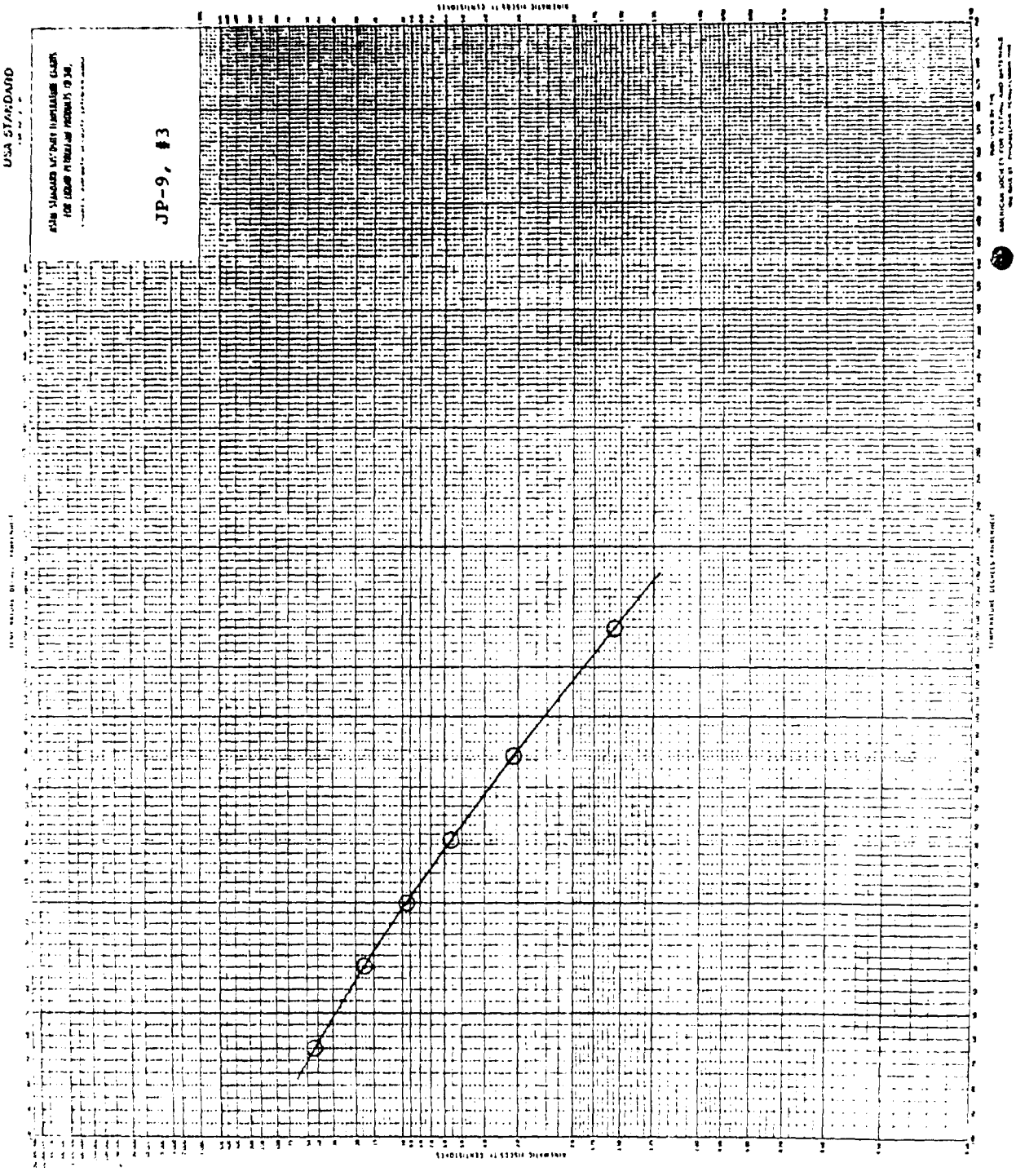

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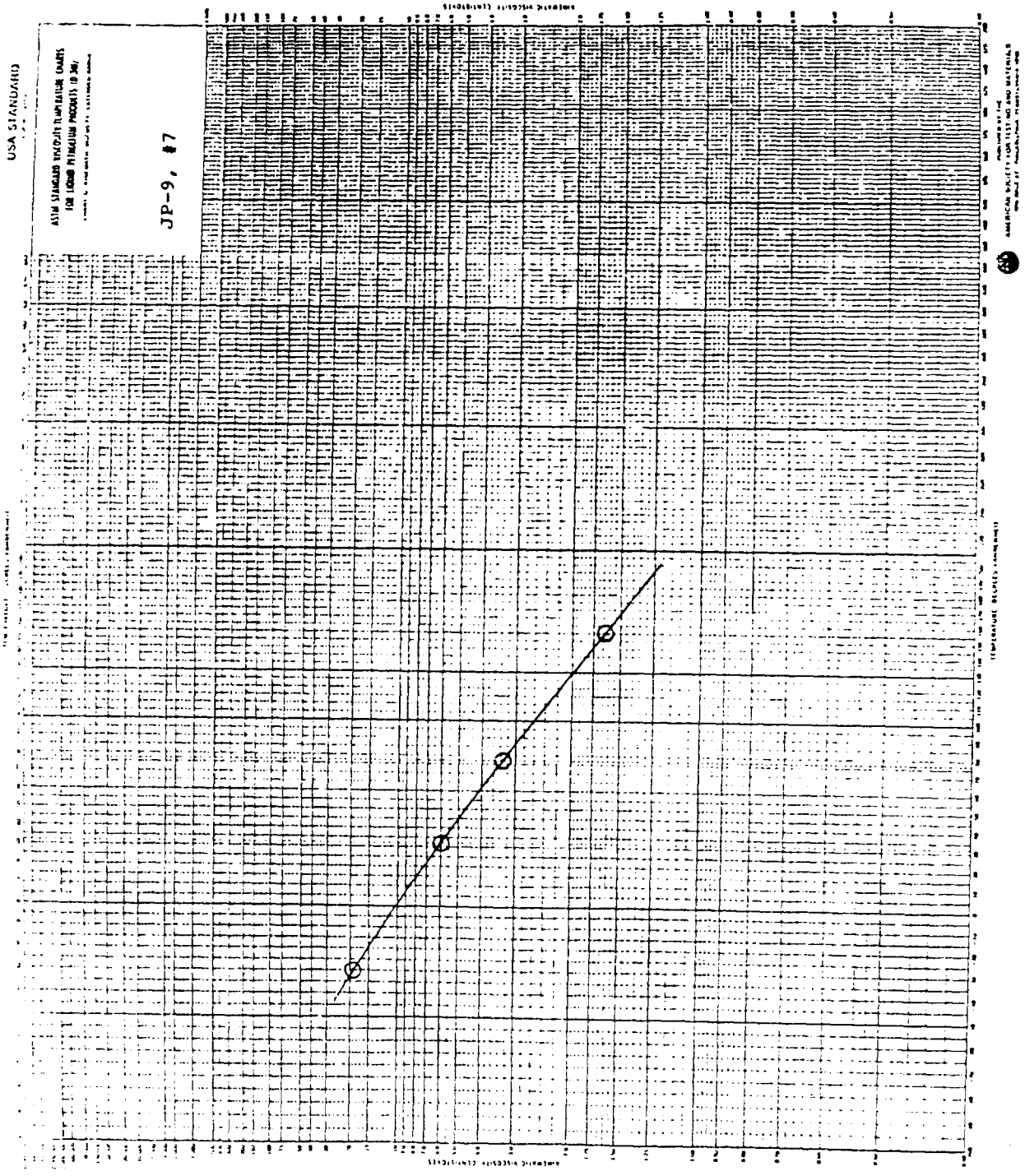
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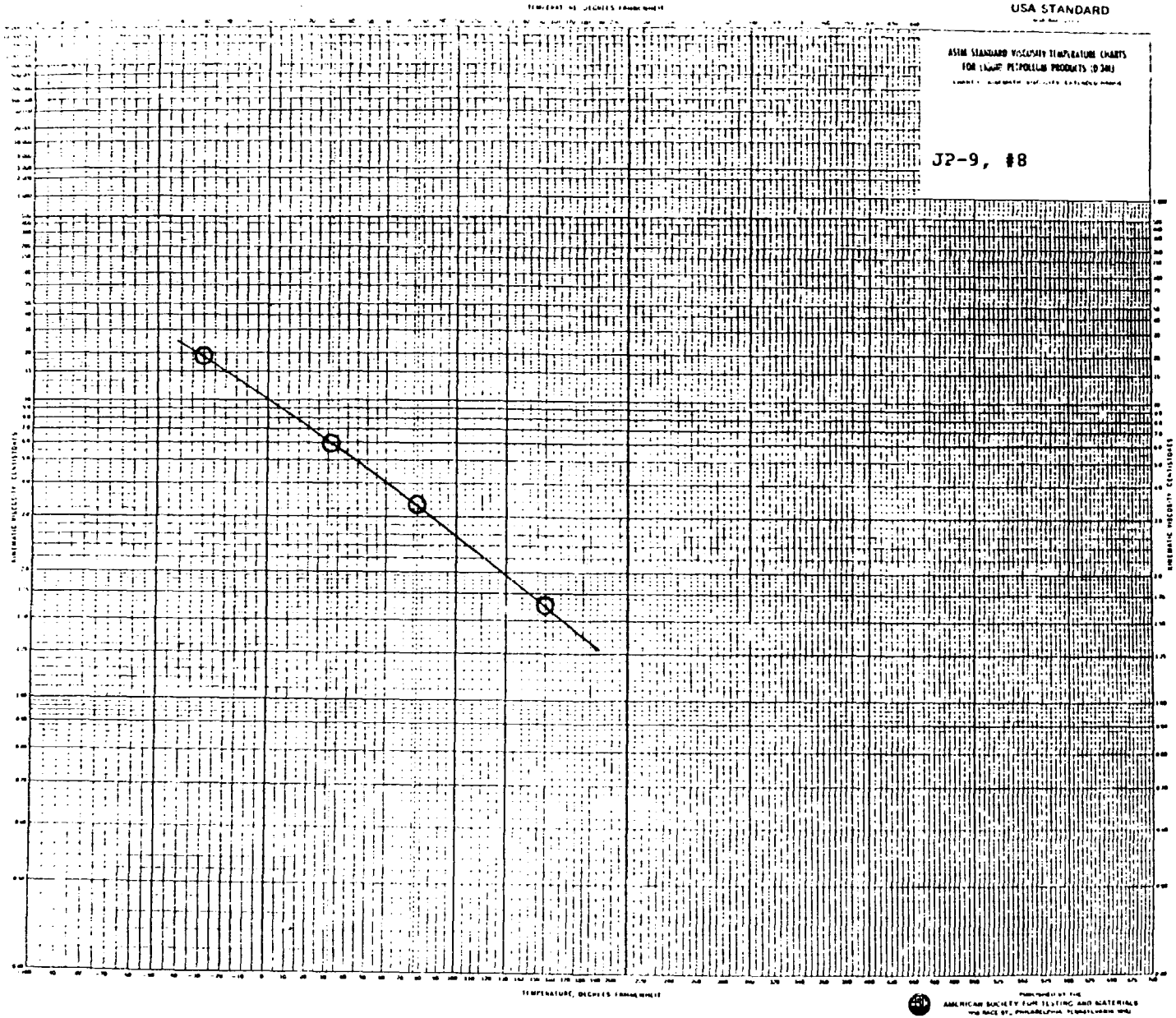
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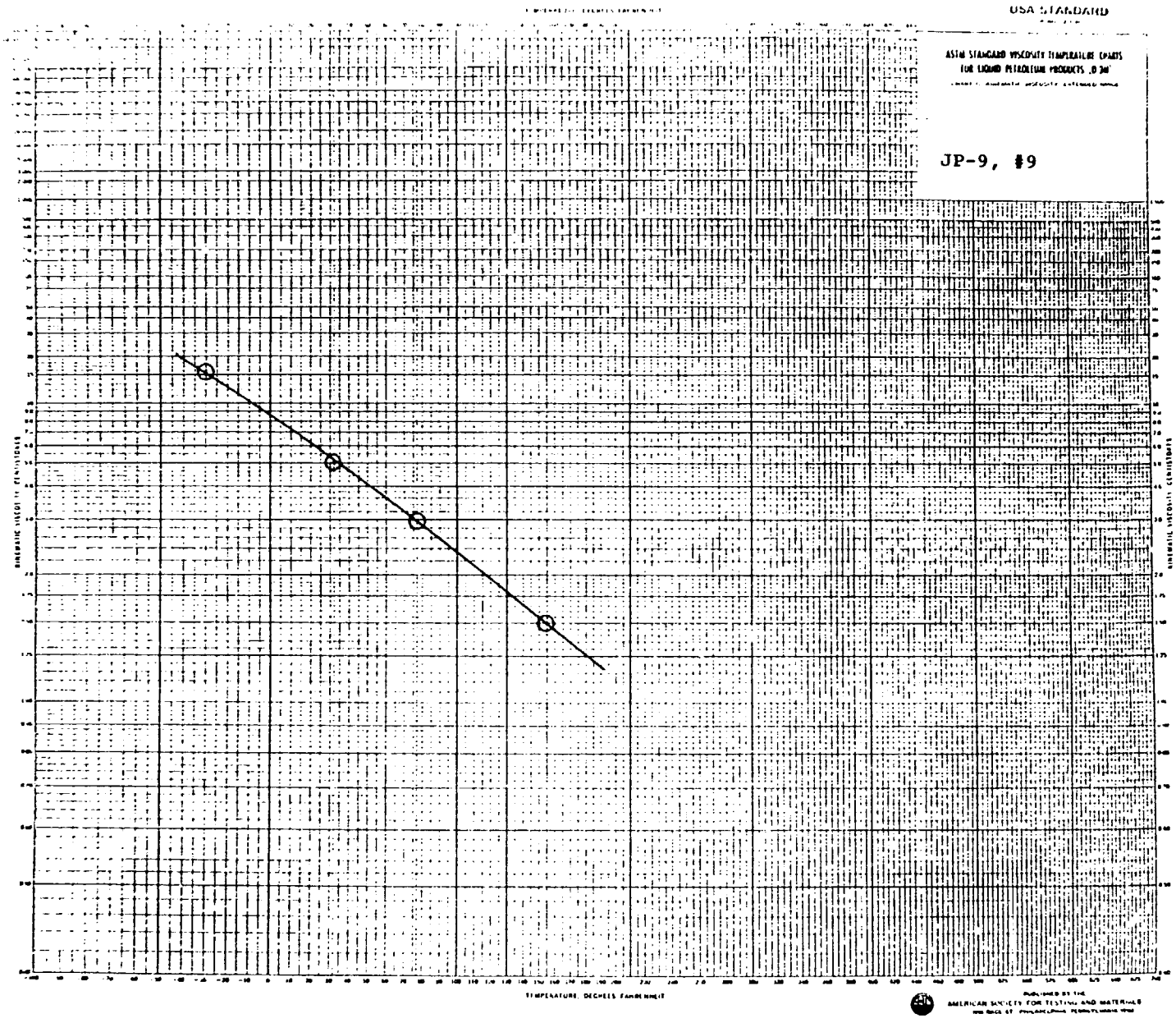
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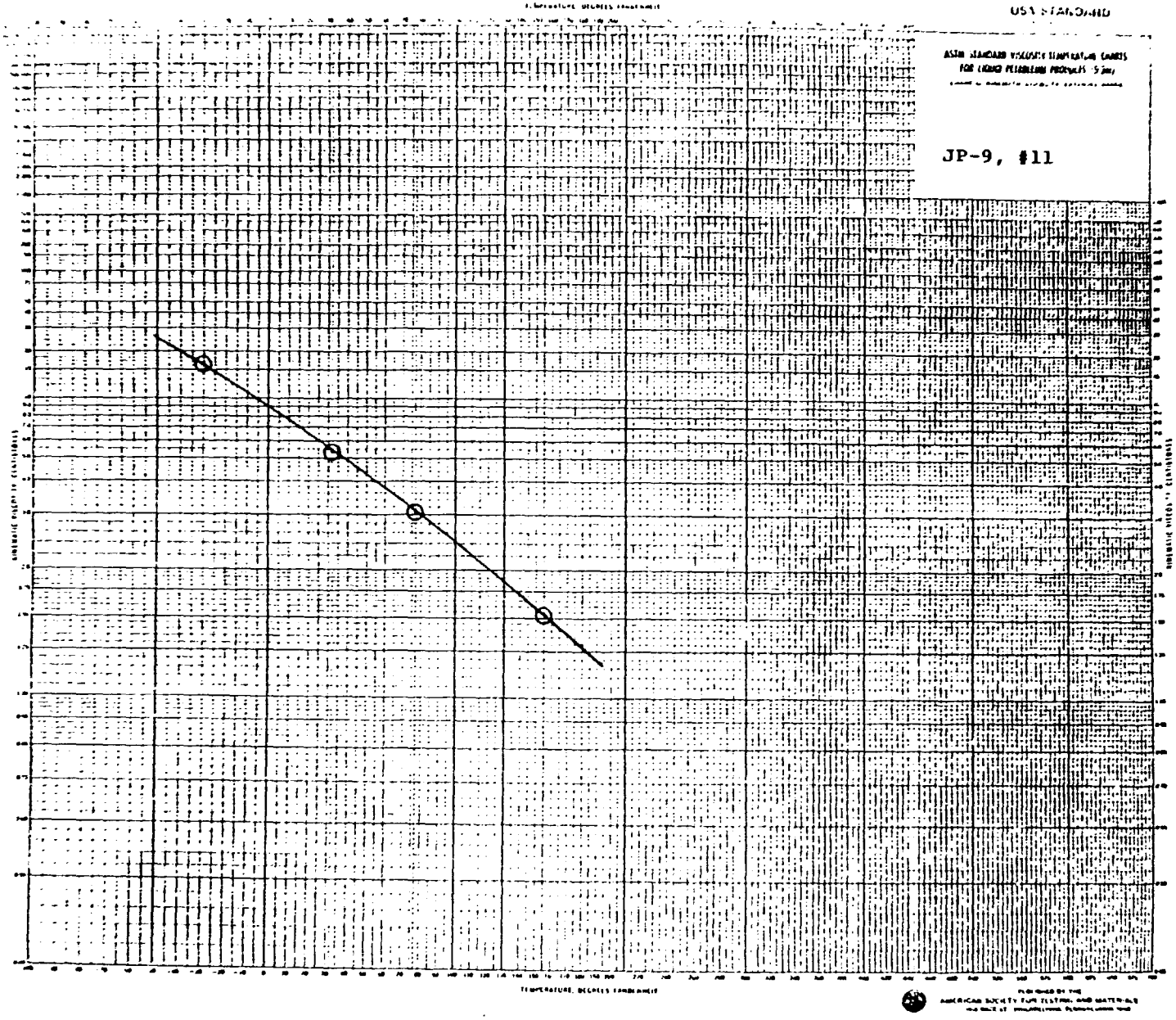
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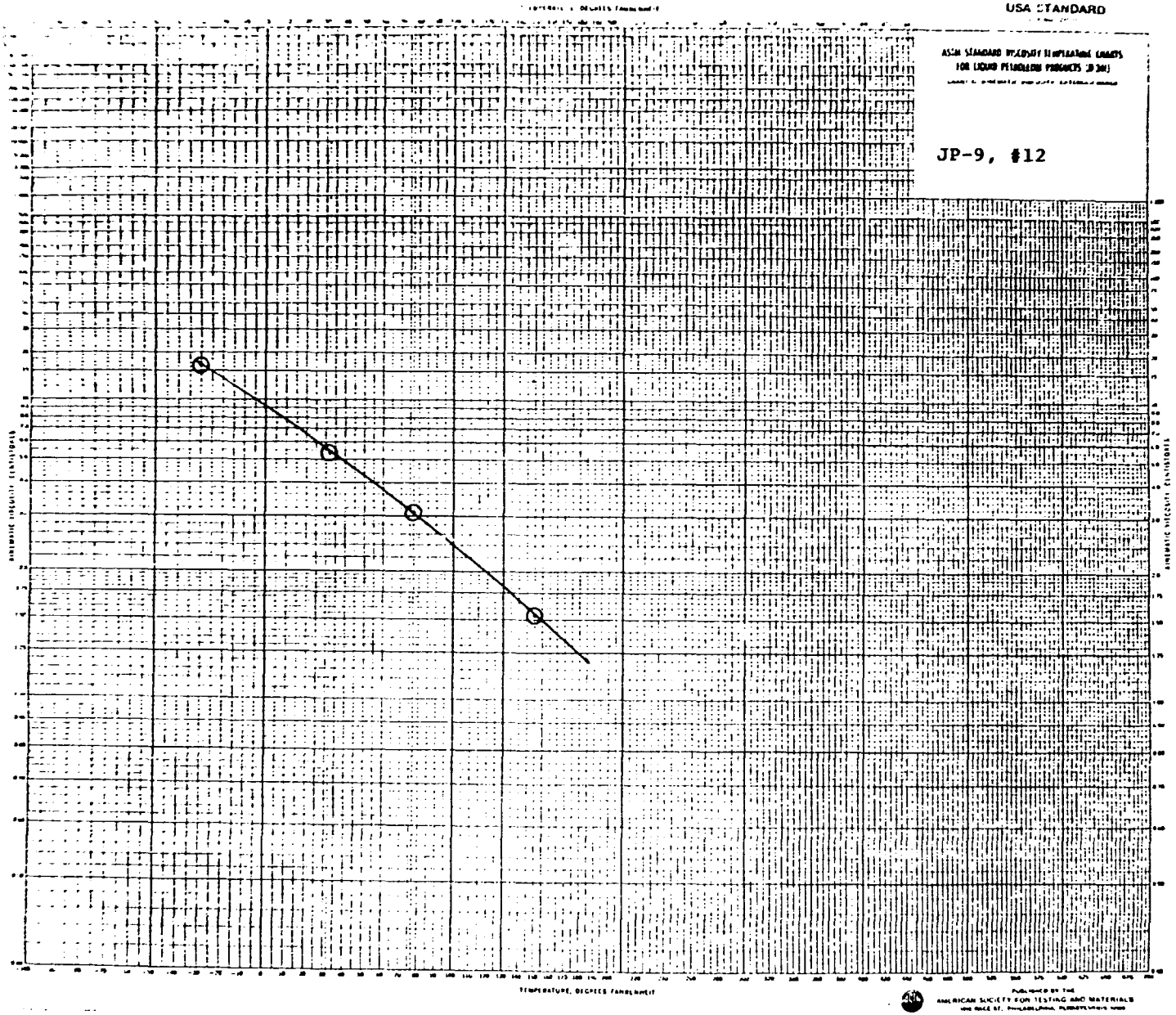
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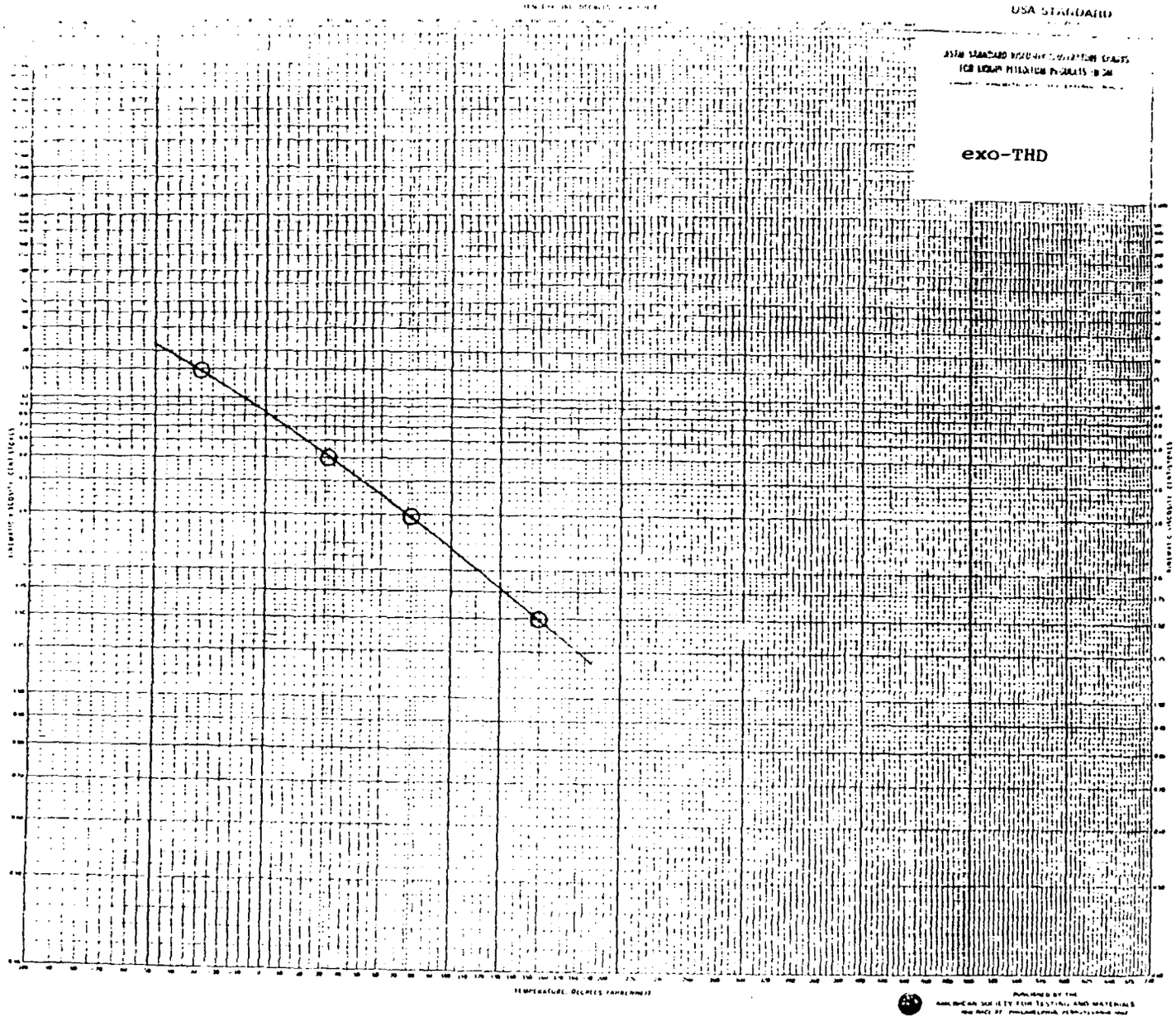
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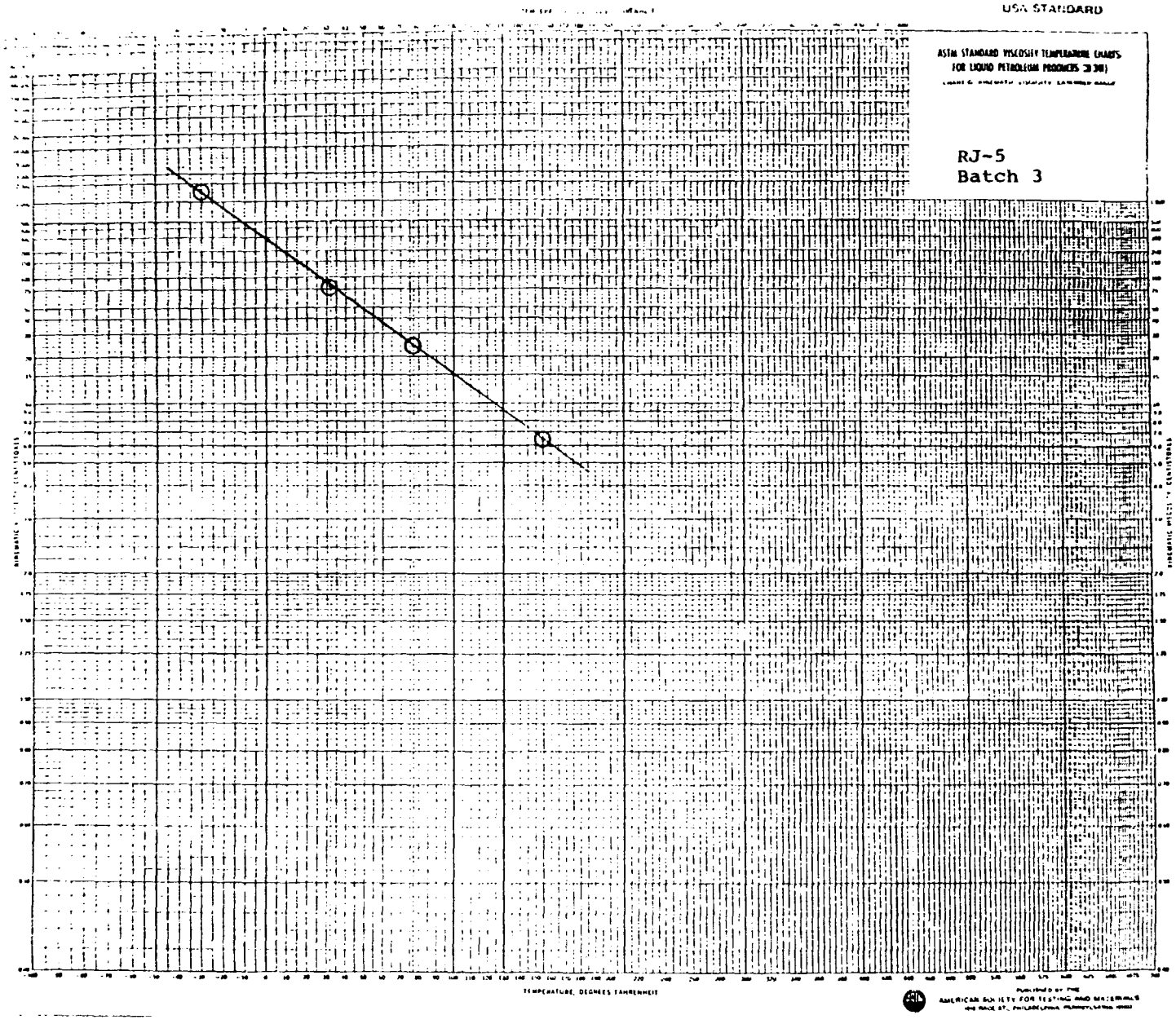
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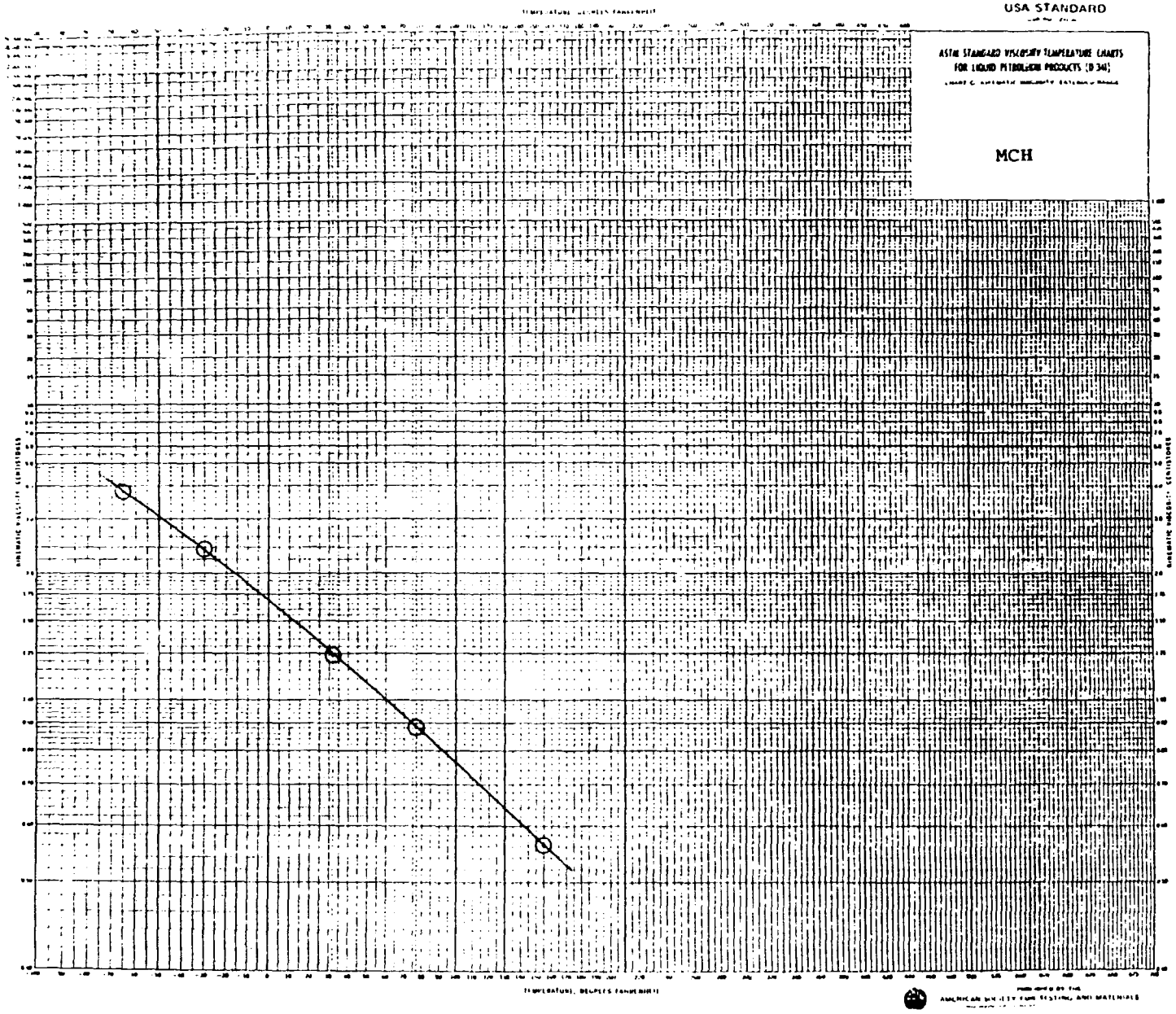
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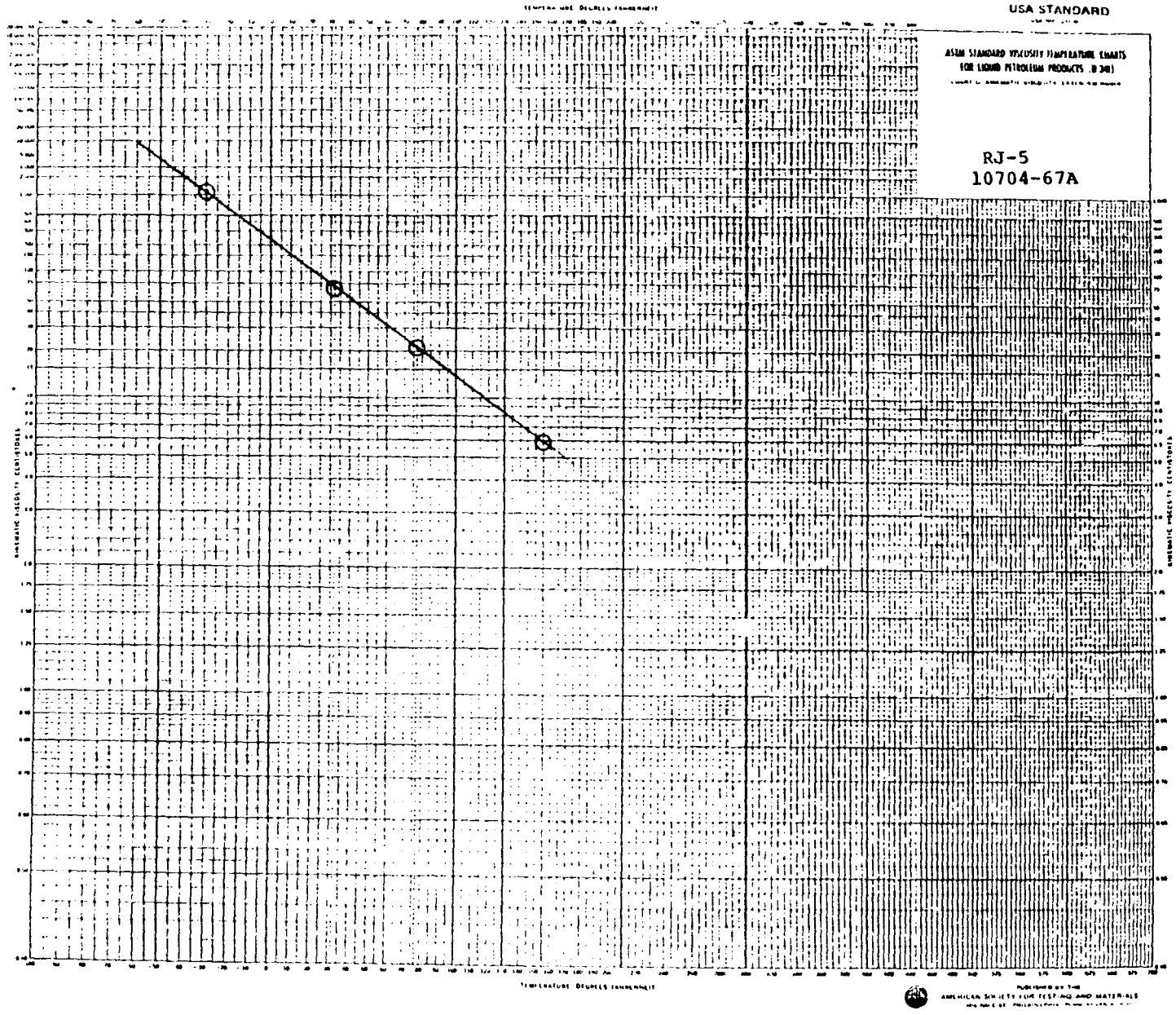
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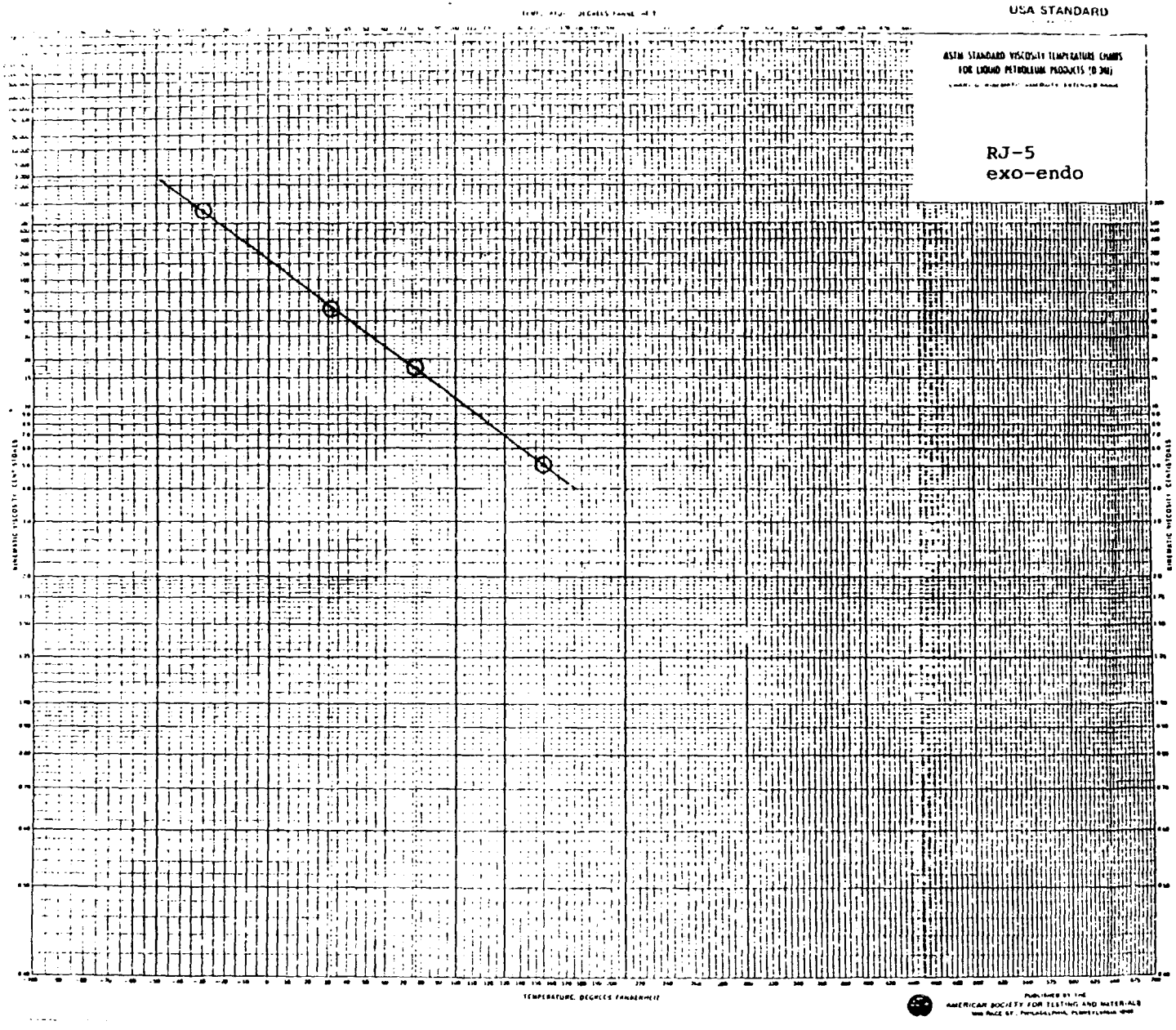
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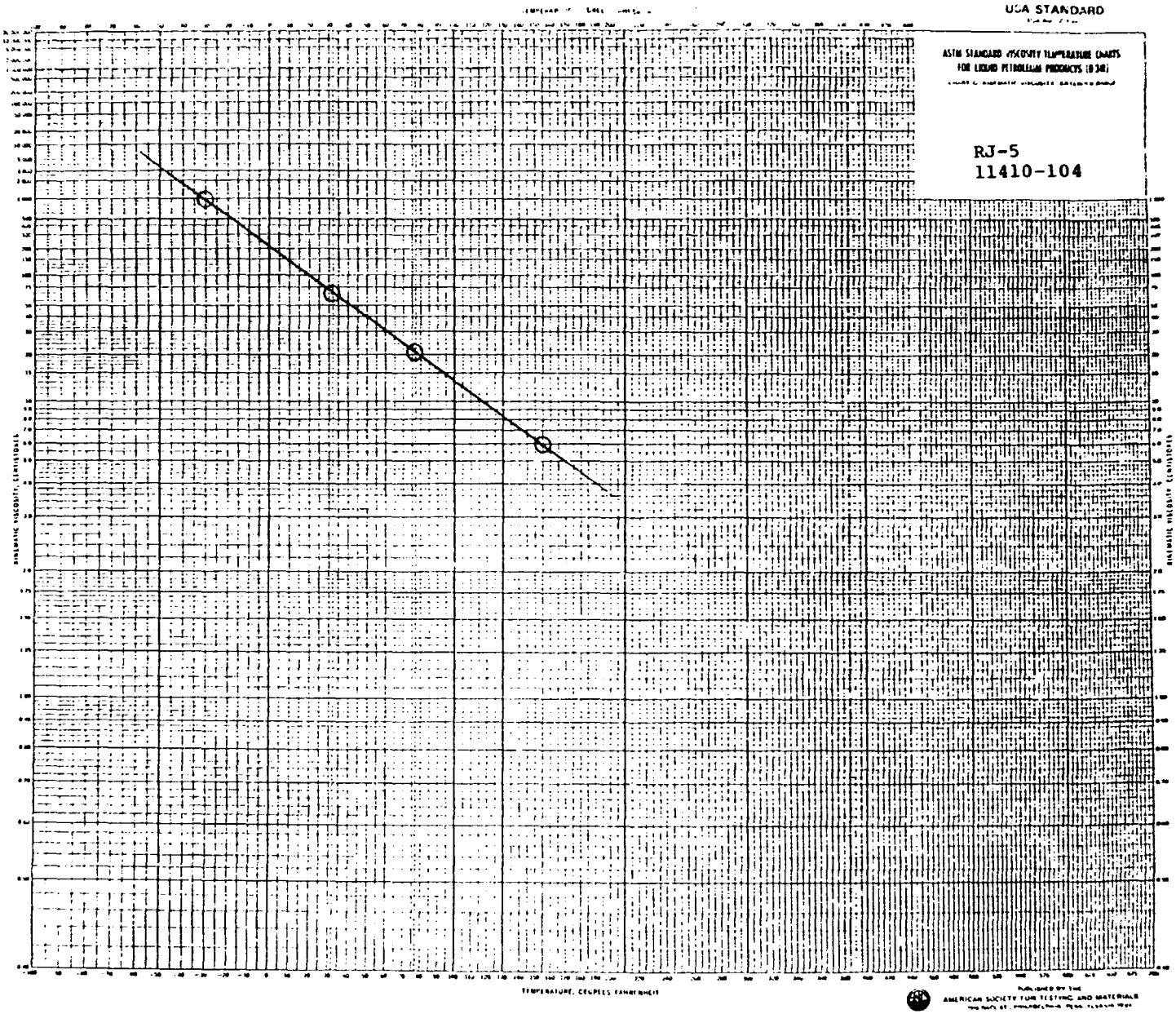
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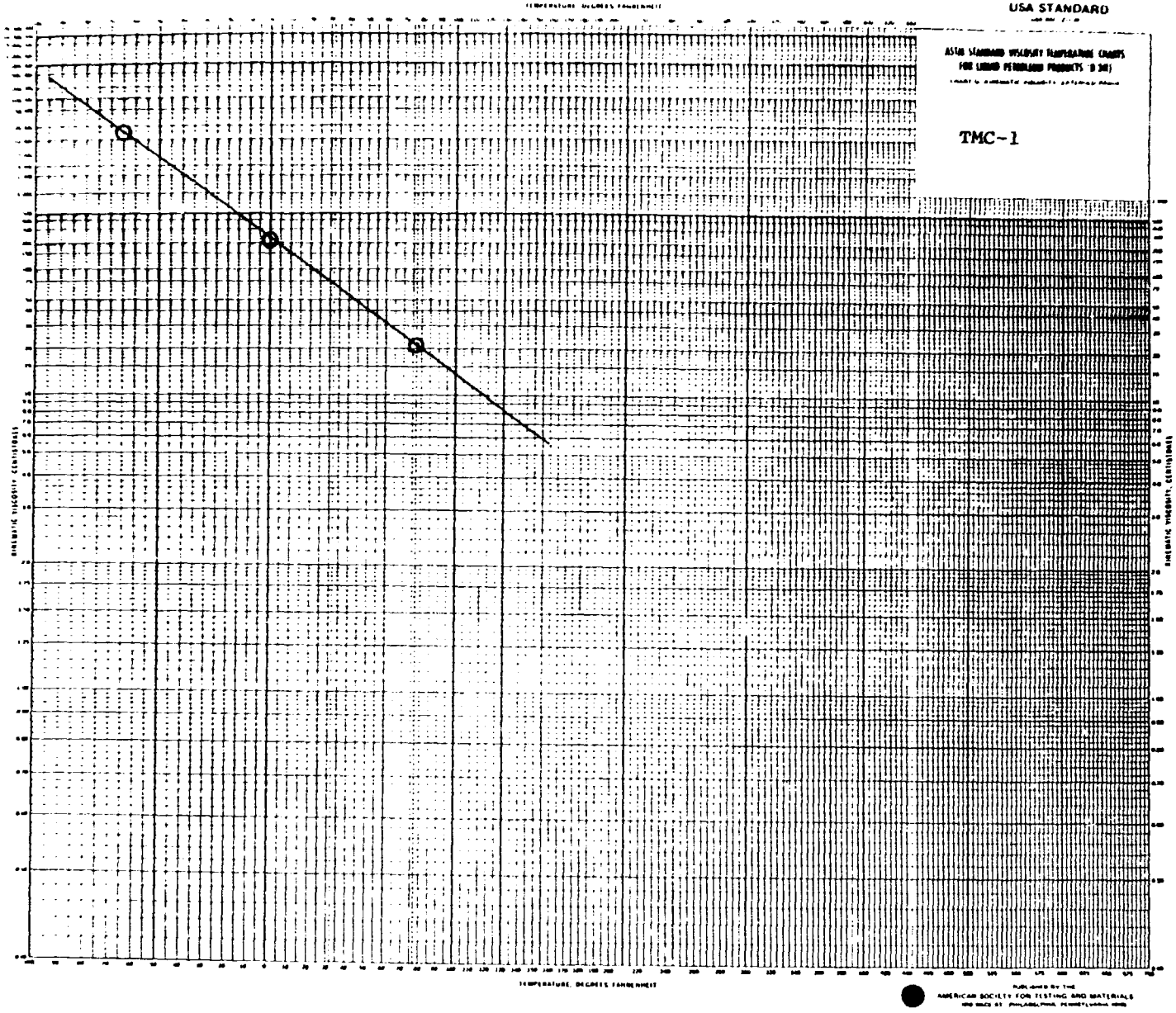
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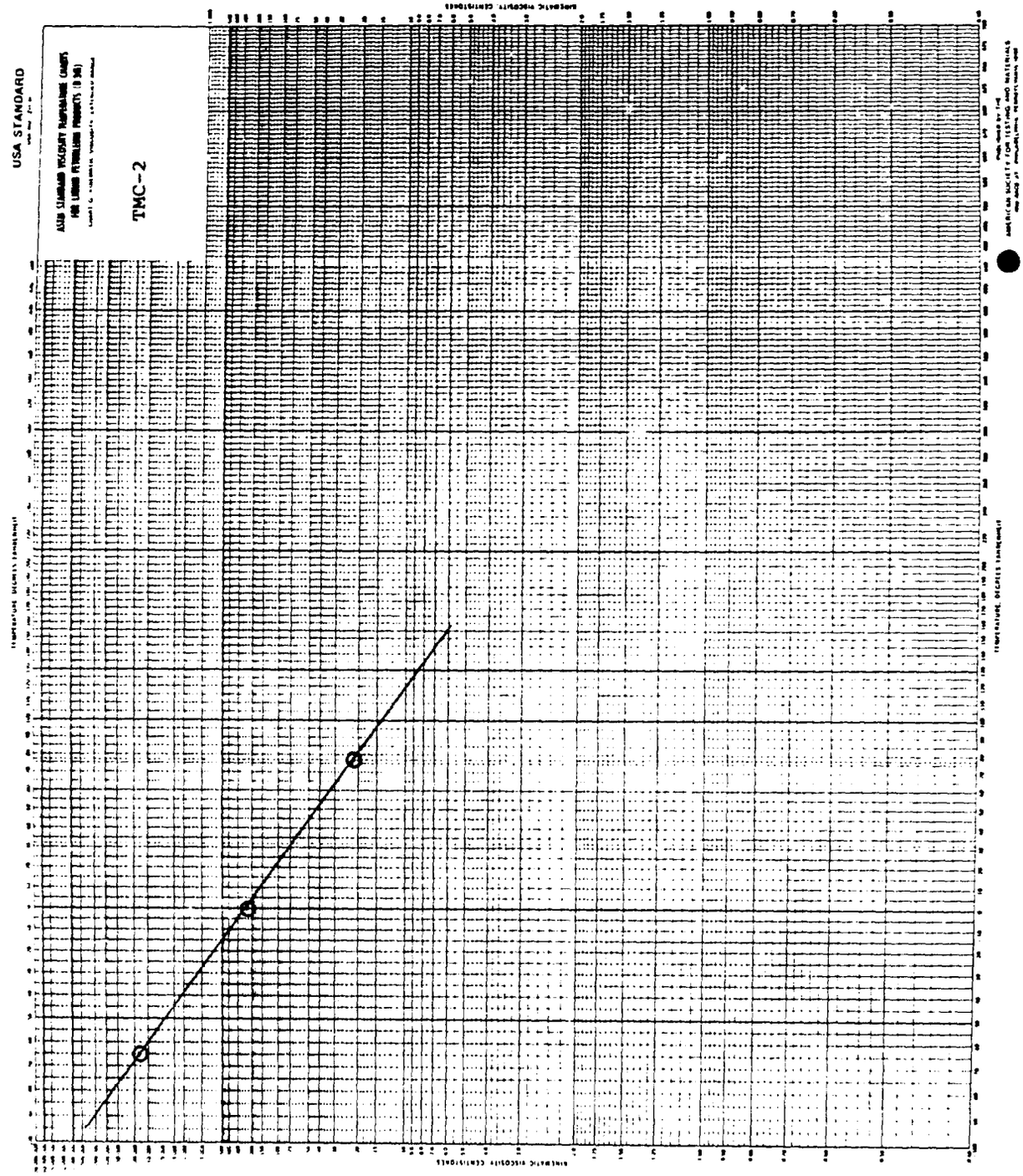
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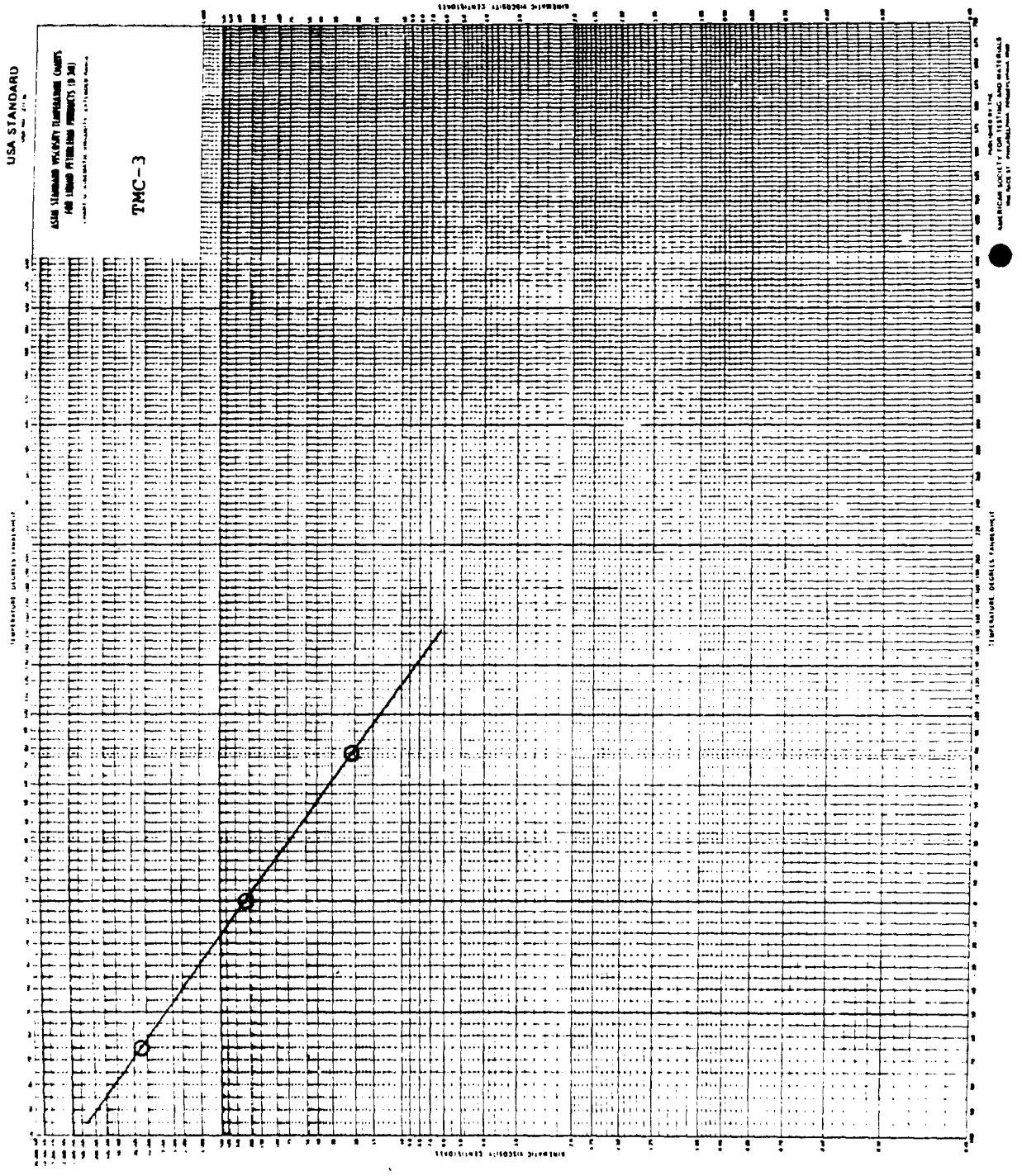
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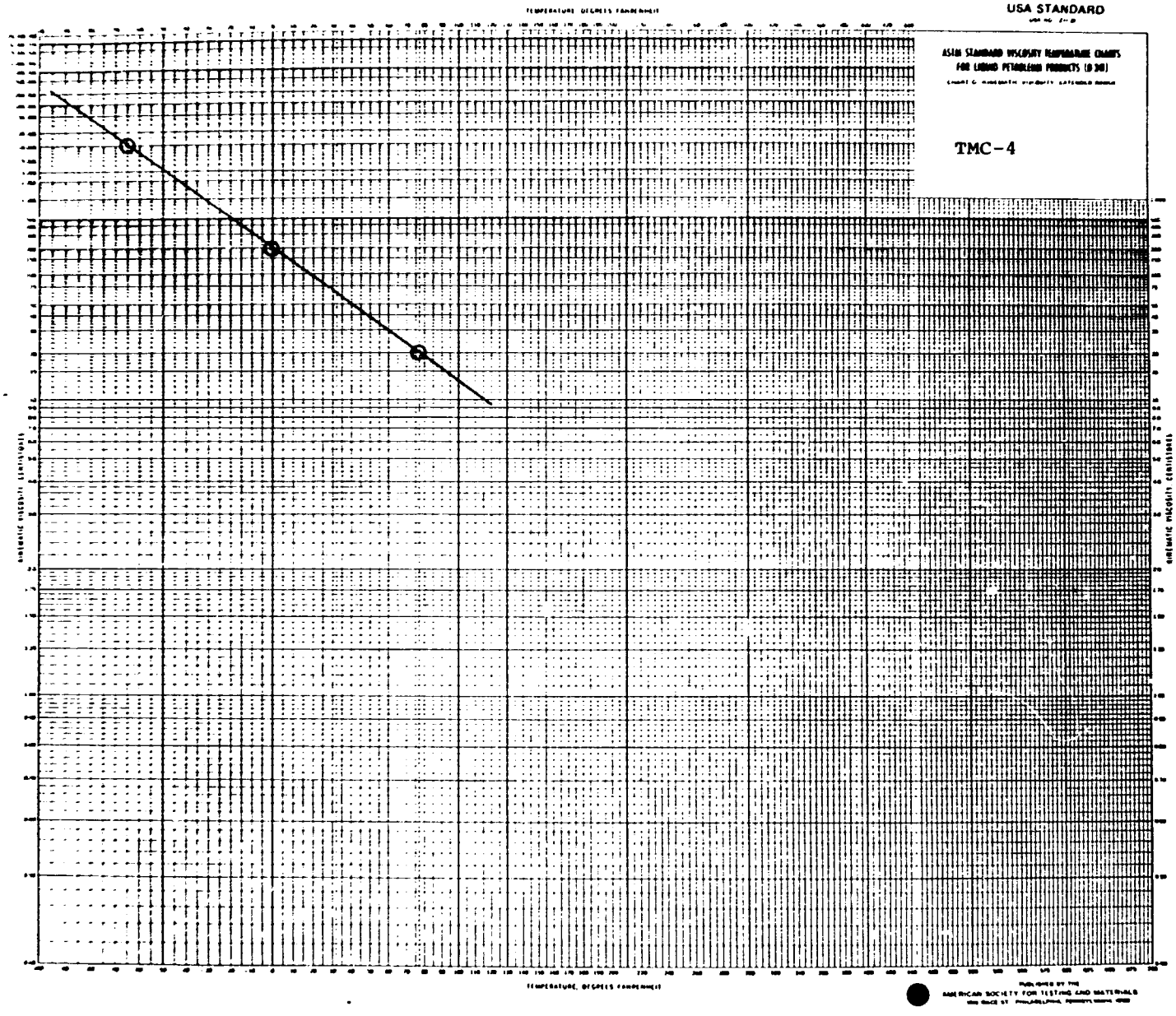
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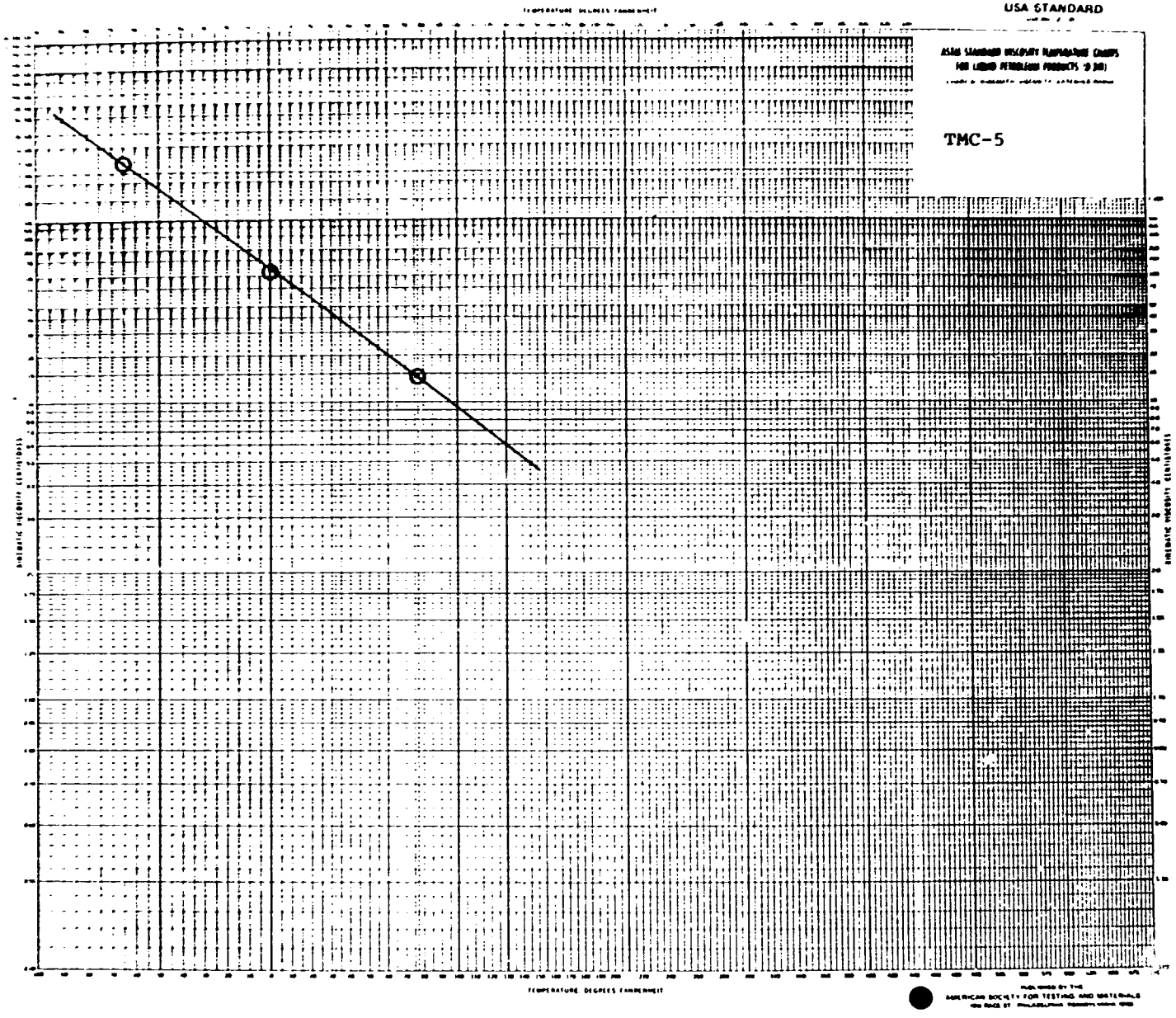
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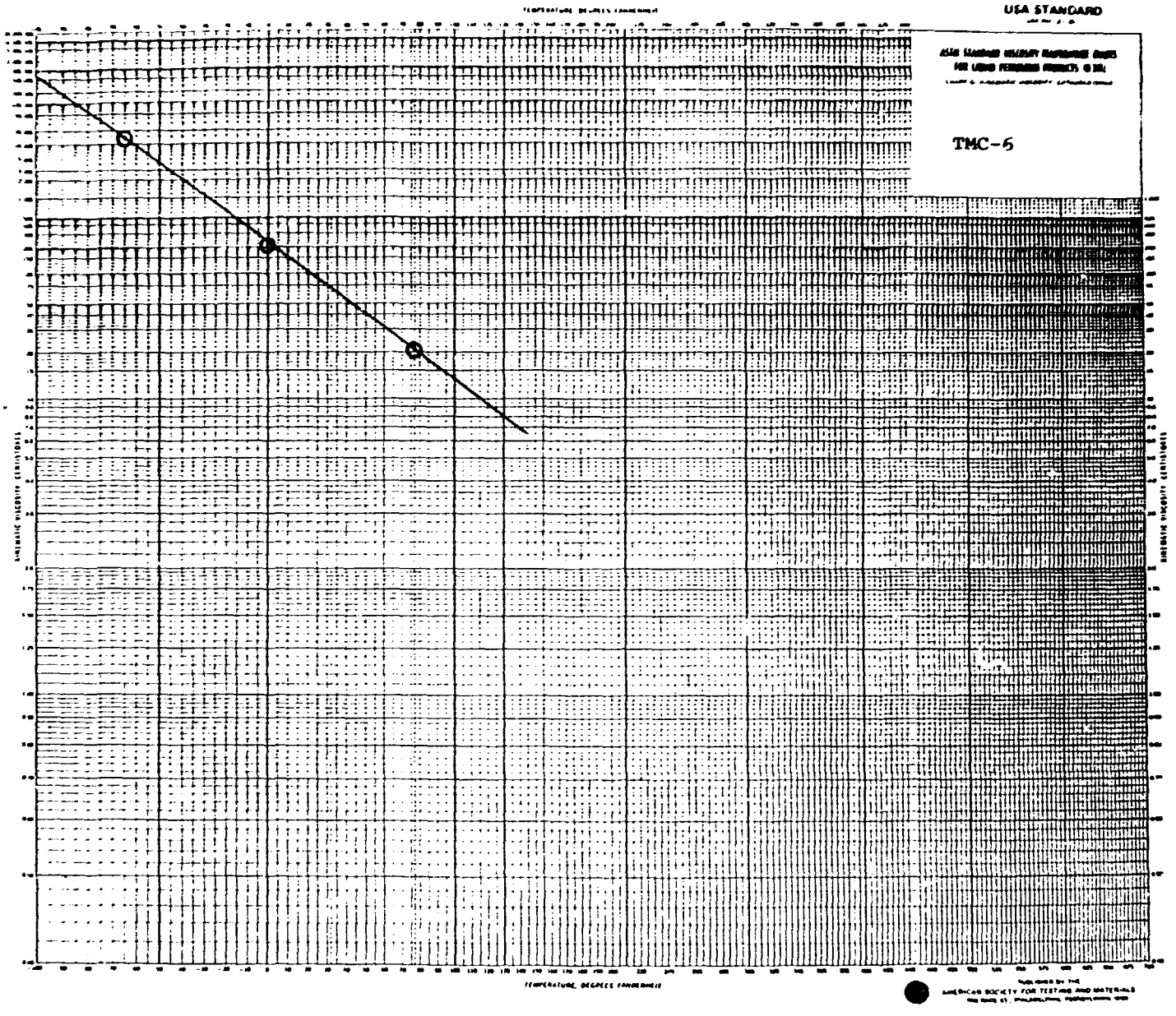
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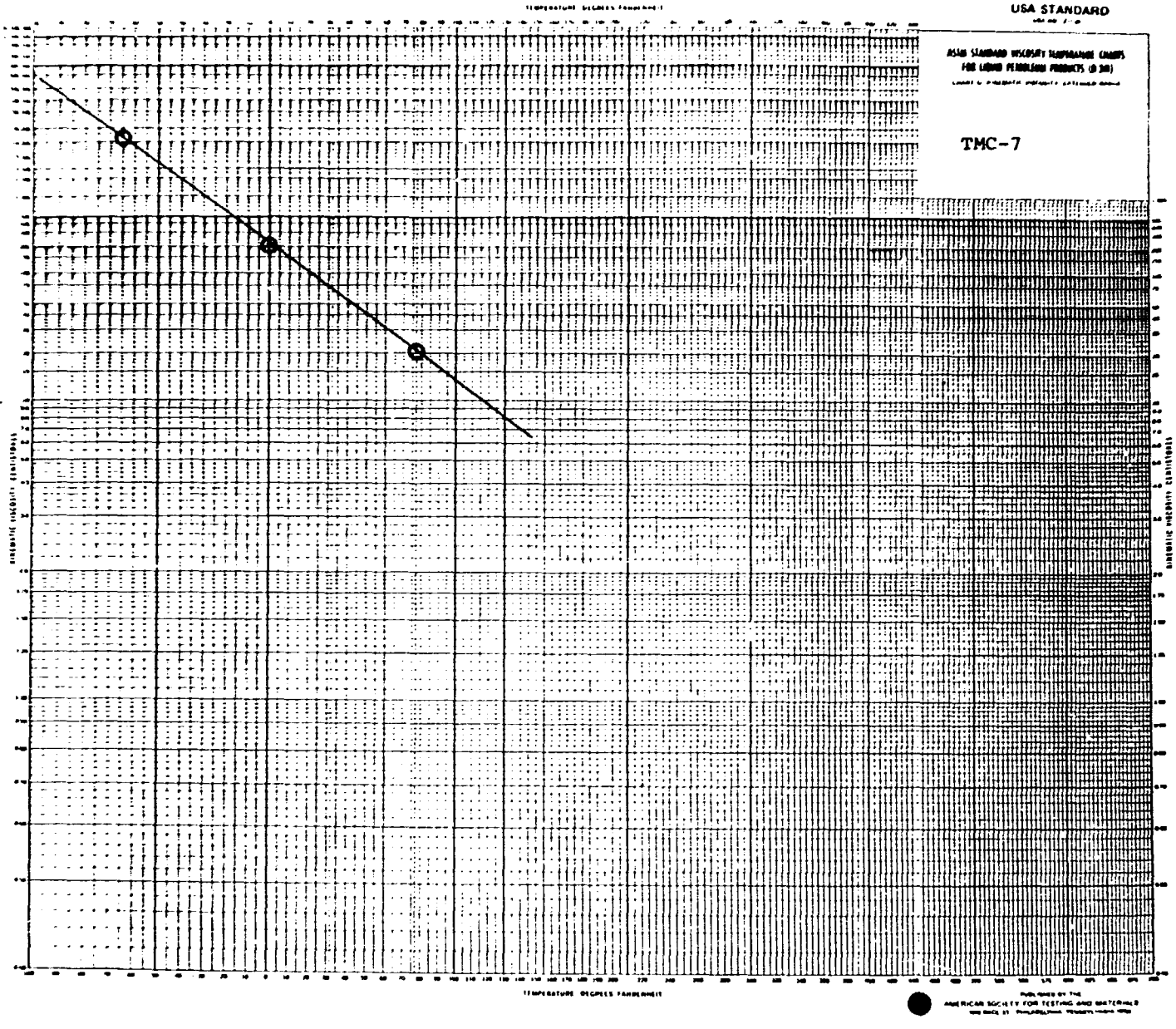
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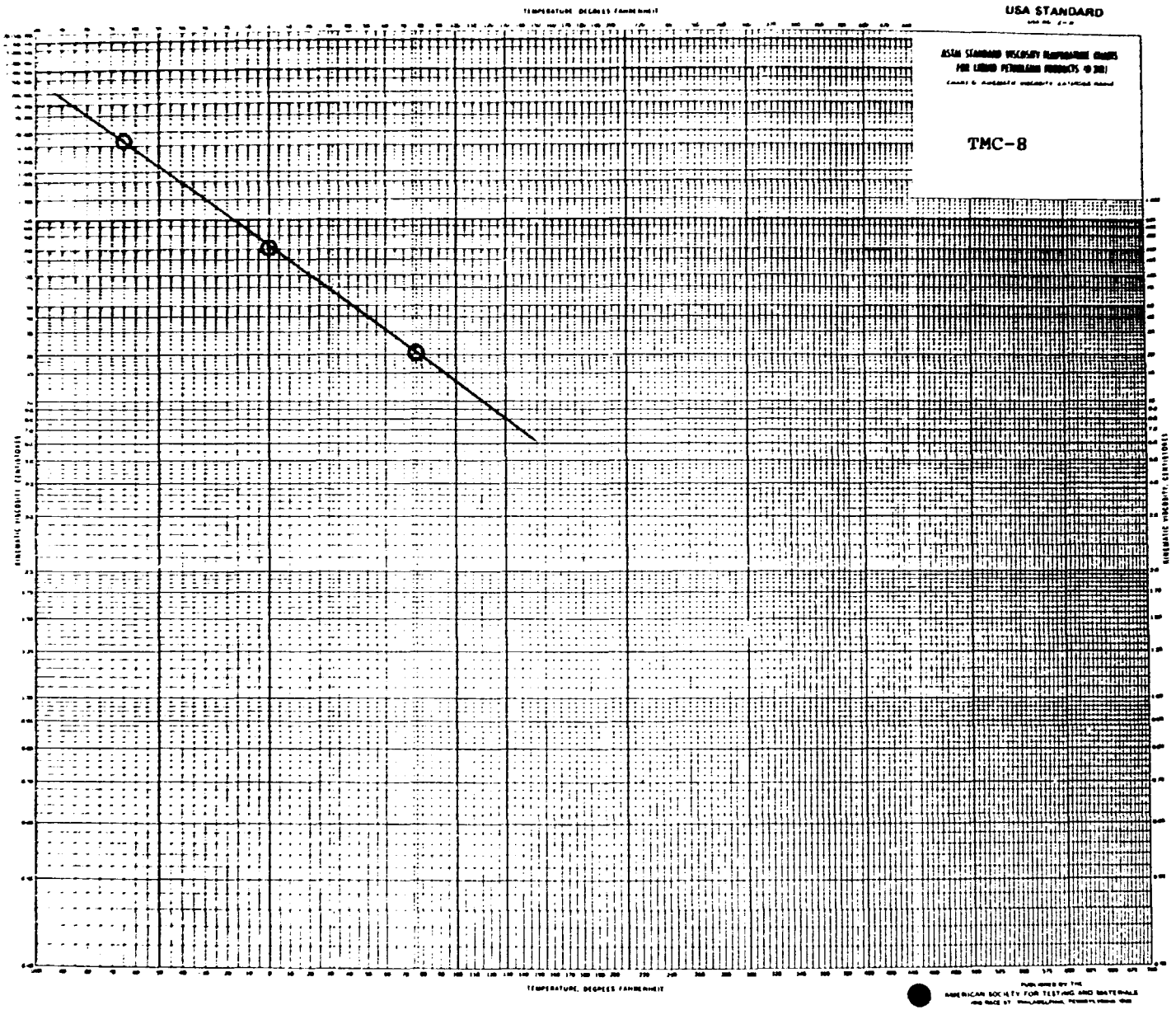
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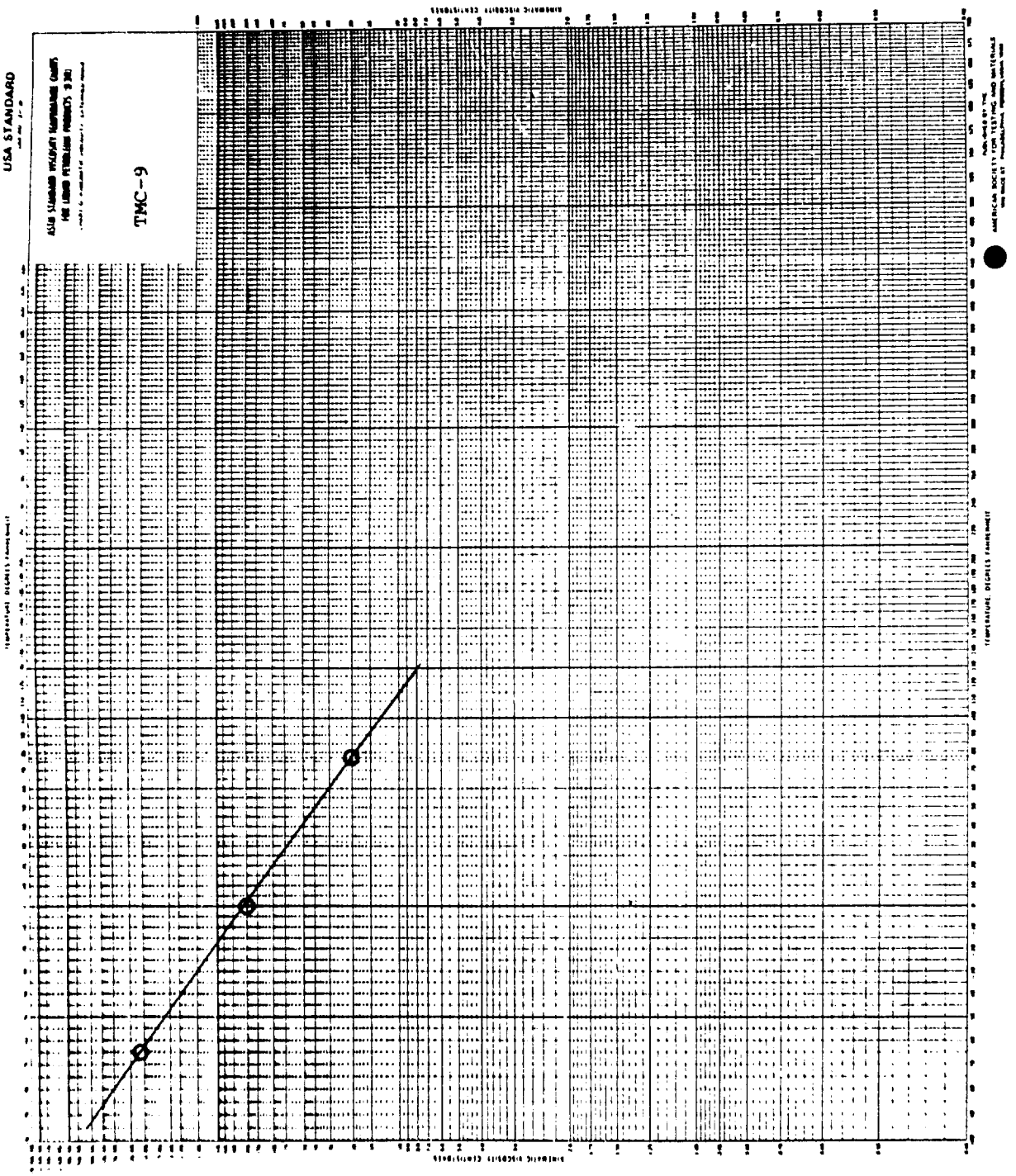
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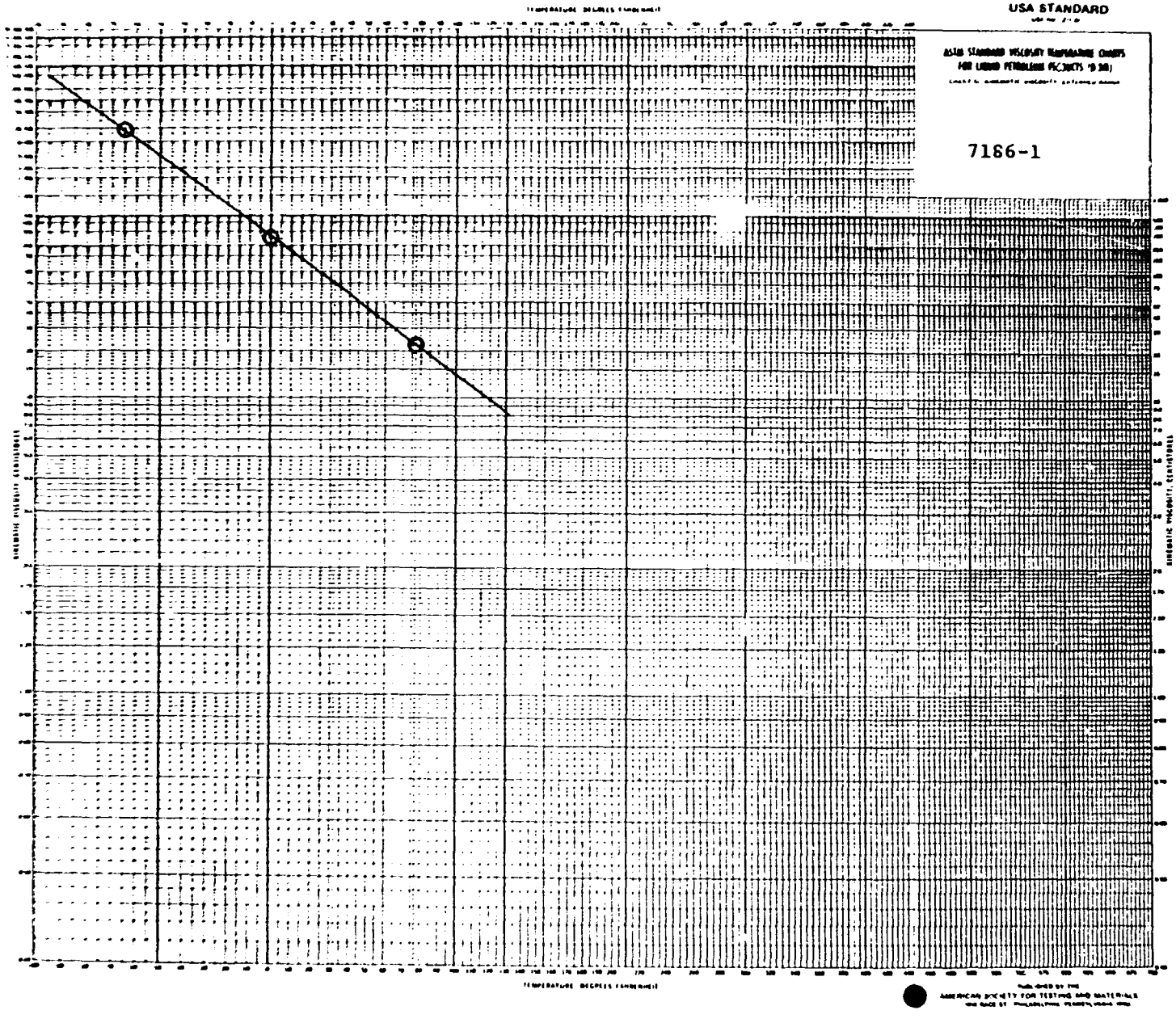
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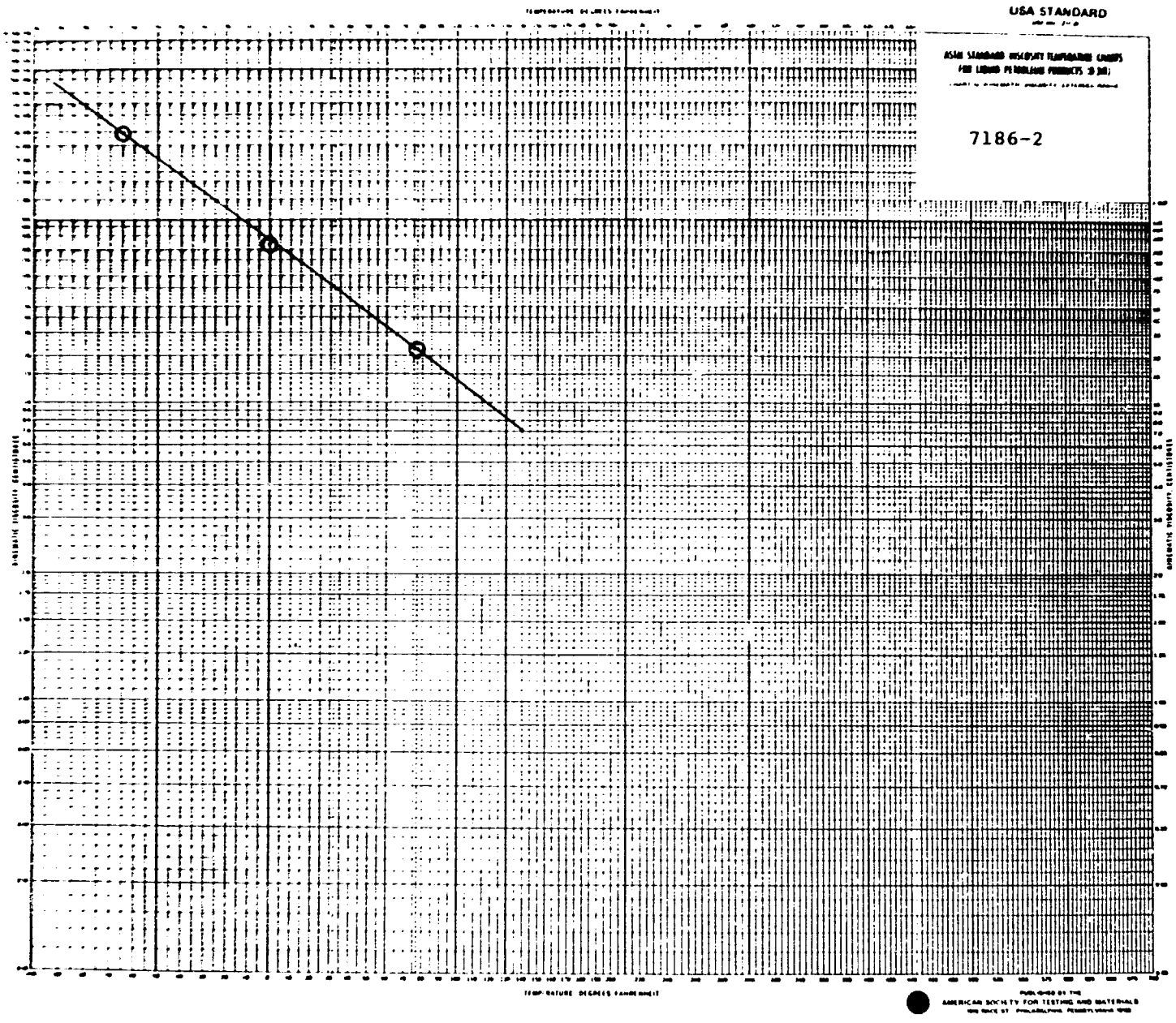
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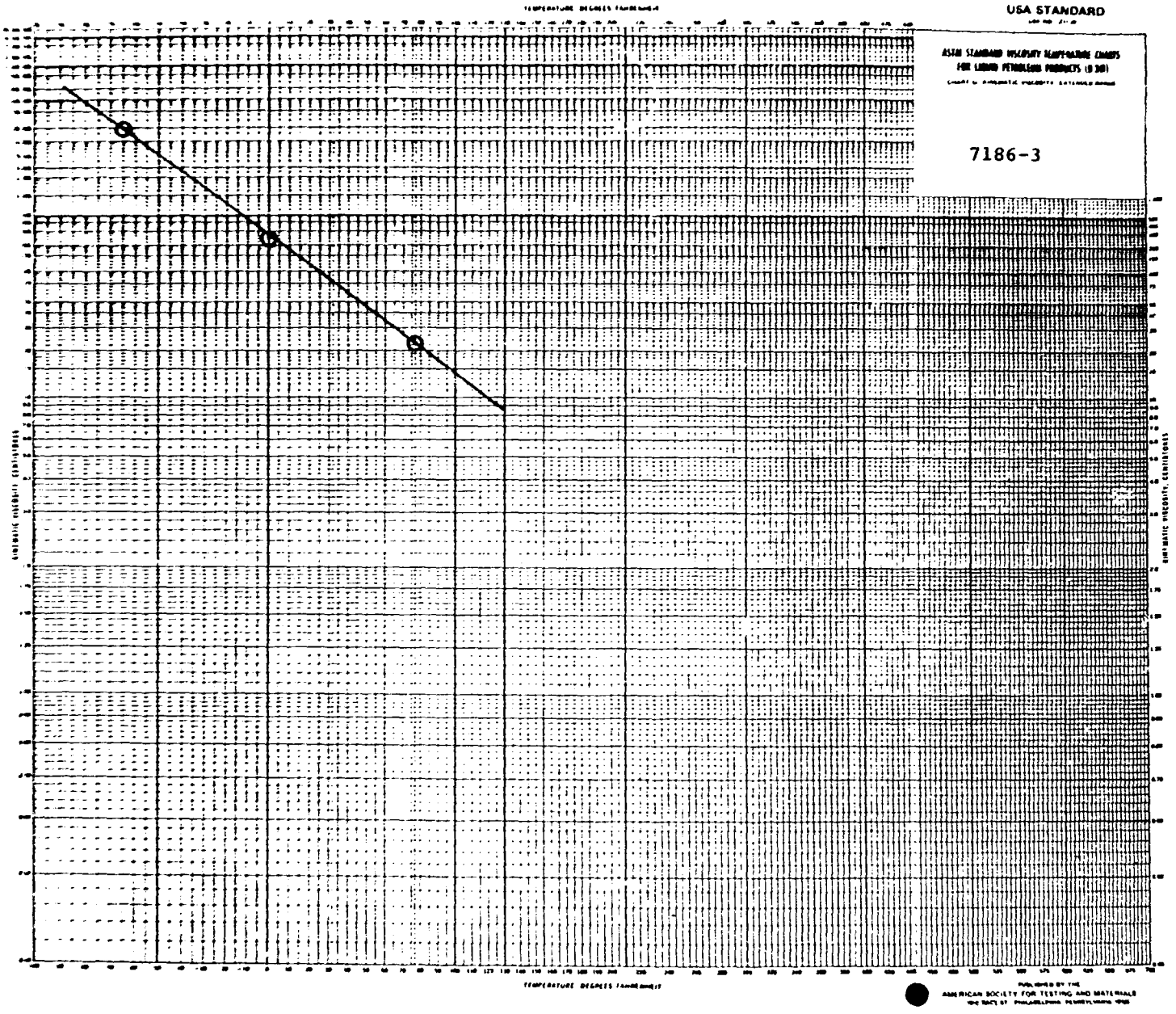
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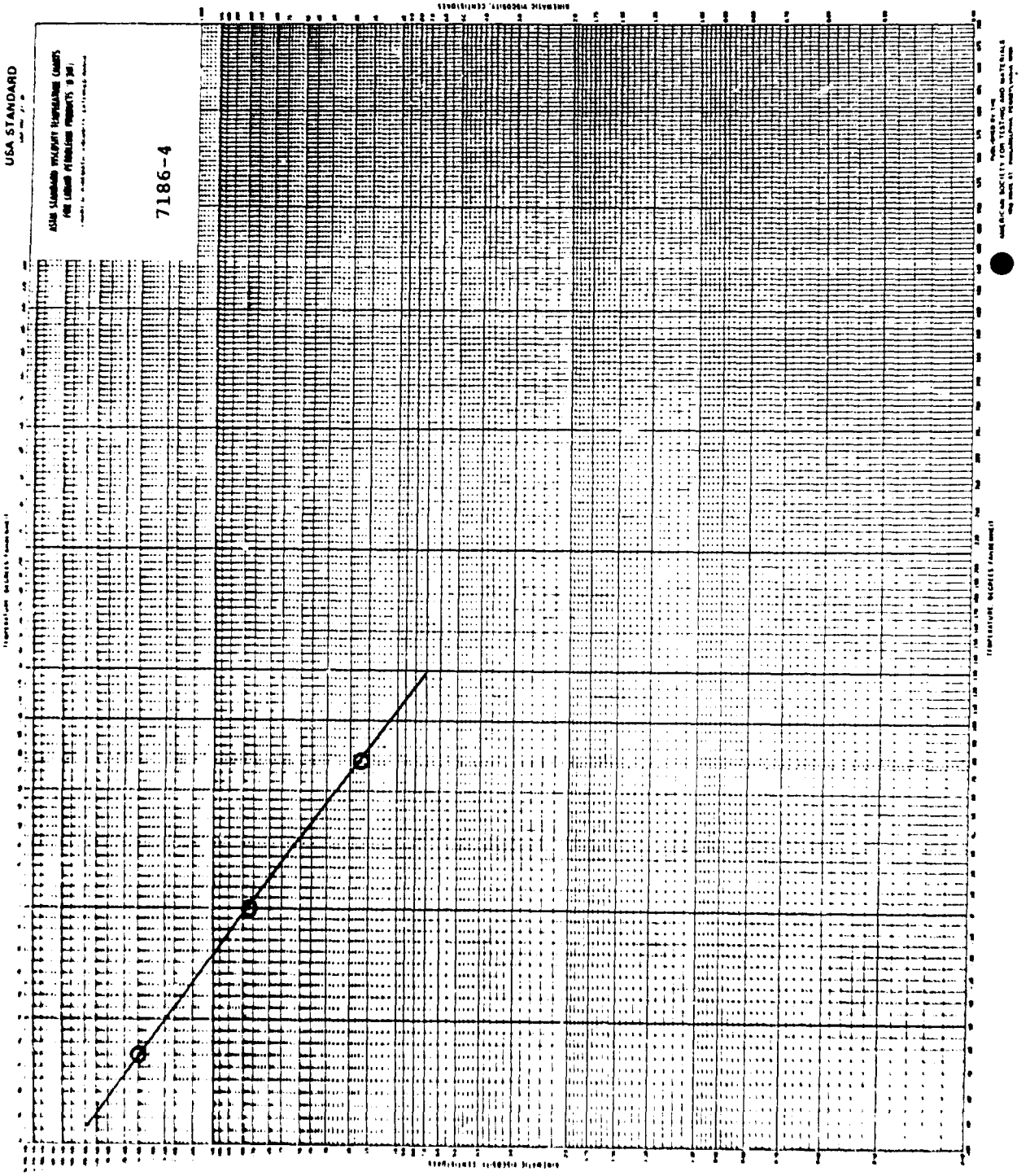
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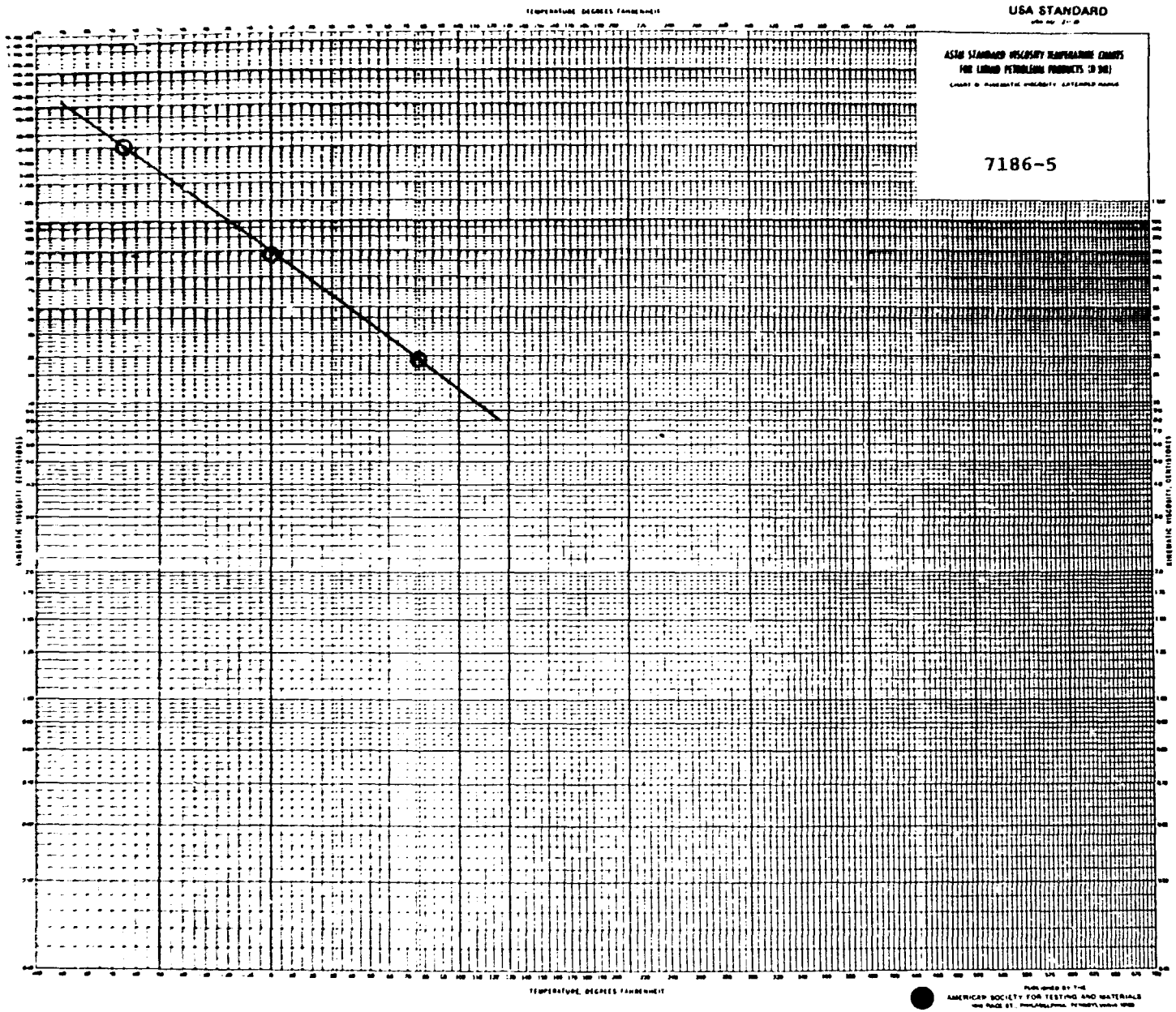
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KINEMATIC VISCOSITY, CENTISTOKES
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APPENDIX B

SPECIFIC MEASUREMENT TECHNIQUES

APPENDIX B

SPECIFIC MEASUREMENT TECHNIQUES

A. GAS CHROMATOGRAPHIC ANALYSIS

Many of the gas chromatographic analyses conducted on JP-9 and other fuels employed the same instrument and similar analytical conditions.

A Perkin-Elmer Model 3920B gas chromatograph having a 50-meter x 0.01 inch glass open tubular column coated with SF-96 stationary phase was used as indicated. Other parameters were:

Detector type - Flame ionization
Carrier gas - Helium
Flow rate - 3 ml/min
Typical Temperatures Program - Column initially 60°C - held for 4 min
Program Rate - 8°C/min
Final temp. - 180°C
Injection port - 300°C

Data were recorded and processed using a Hewlett-Packard 3350 laboratory data system in most cases.

B. MEASUREMENT OF AIR AND NITROGEN SOLUBILITY

The solubility of air or nitrogen at saturation were measured by a mass spectrometric technique. The fuel was saturated with air in a distillation flask to which a reflux condenser was attached. The flask was placed in a constant temperature bath maintained at the desired temperature. A fritted-glass gas dispersion tube was immersed into the fuel through which CGA

Grade E compressed breathing air or nitrogen was passed. Water from an ice bath was circulated through the jacket of the condenser by means of a small pump. This procedure prevented loss of volatile components during saturation of the fuel.

For analysis, an apparatus consisting of a degassing chamber followed by a cold trap was attached to the bulk gas inlet of a 21-103 C mass spectrometer. The vacuum system which is a part of the inlet unit was used to facilitate specimen degassing. The sample was continuously agitated during the degassing period. Samples of known weight were measured with instrument calibration being achieved by the measurement of known volumes of air. The determined value for air is independent of the amount of hydrocarbons in the vapor.

C. METHOD FOR SURFACE TENSION

All surface tension measurements presented in this report were conducted by the capillary-rise method. Surface tension is given by the expression:

$$v = \frac{rhdg}{2 \cos \theta}$$

where d is the density of the liquid
h is the height of the column of liquid
g is the acceleration of gravity in cms per sec
r is the radius of the capillary in cms
θ is the contact angle

The force due to surface tension acts at the contact angle, θ, with the vertical. For most liquids which wet glass, the angle, θ, is essentially zero and cos θ equals 1.

If wetting of the glass is poor, contact angles must be measured. A Gaertner contact-angle goniometer was used for the purpose.

The numerical value of the gravitational factor used in calculations is 980.08. Capillary radii were determined using both distilled water and benzene as reference fluids. The height, h, of the fluid column above the surface of the liquid was measured by means of a Gaertner Scientific Corp. cathetometer.

REFERENCES

1. Trump, W. N., Rev. Sci Instrum, 48(1) No. 1, January 1977.

2. Gallant, R. W., "Physical Properties of Hydrocarbons", Volume 1, pp. 142.

3. Toulockian, Y. S., "Thermochemical Properties of Matter", TRRC Data Series, Vol. 6, pp. 266.

4. Mottlau, A. Y. Anal. Chem. 29, 1196 (1957).

5. "Analytical Methods for Atomic Absorption Spectrometry", Perkin Elmer Corp., Norwalk, Conn. (Sept. 1976).

6. Appendix C, Mil-T-38219A, 14 June 1977. Military Specification, Turbine Fuel, Low Volatility, JP-7.

7. MAL Report No. 3082, Bendix Aerospace Systems Division, 22 December 1977.

8. Dushman, S., Vacuum Techniques, 2nd Edition. Chapman-Hall. London (1962).

9. "New Concept in Fluorimeter Design", G. K. Turner Associates, Palo Alto, California (1961).

10. American Society Testing Materials, "Hydrocarbon Analysis" STP 389 (1965).

11. Brown, R. A., Anal. Chem., 23, 430-437 (1951).

12. Friedel, R. A., Appl. Spectroscopy 6, 24 (1952).

13. Lumpkin, H. E., B. W. Thomas and A. Elliott, Anal. Chem., 24, 1389 (1952).

14. Clerc, R. J., A. Hood and M. J. O'Neal, Anal. Chem, 27, 868 (1955).

15. Crable, G. F., and N. D. Coggeshall, Anal. Chem., 30, 310 (1958).

16. Hastings, S. H., B. H. Johnson and H. E. Lumpkin, Anal. Chem., 28, 1242-1247 (1956).

17. Robinson, C. J., and G. L. Cook, Anal. Chem., 41, 1548-1554 (1969).

18. Robinson, C. J., Anal. Chem., 43, 1425-1434 (1971).

19. Lumpkin, H. E., Anal. Chem., 36, 2399 (1964).

20. Yew, F. F., and B. J. Mair, Anal. Chem., 38, 231 (1966).

21. Johnson, B. H., and T. Aczel, Anal. Chem., 39, 682 (1967).

22. Williams, R. B., Symposium on Composition of Petroleum Oils, Determination and Evaluation, ASTM Special Technical Publication 224, 168-194 (1958).

23. Brown, J. K., and W. R. Ladner, Fuel (London), 39, 87-96 (1960).

24. Clutter, D. R., Leonidas Petrakis, R. L. Stenger, Jr., and R. K. Jensen, Anal. Chem., 44(8), 1395-1405 (1972).

25. Myers, M. E., J. Stollsteimer, and A. M. Wims, Anal. Chem., 47(12), 2010-2015 (1975).

26. Friedel, R. A., and H. L. Retcofsky, Chemistry and Industry, 455-456 (1966).

27. Knight, S. A., Chemistry and Industry, 1920-1923 (1967).

28. Shoolery, J. N., and W. L. Budde, Anal. Chem., 48(11), 1458-1461 (1976).

29. Wooten, D. L., H. C. Dorn, L. J. Taylor, and W. M. Coleman, Fuel (London), 55(3), 224-226 (1976).

30. Martin, R. L., Anal. Chem., 34(8), 896-899 (1962).

31. Albert, D. K., "Determination of C_5 to C_{11} n-Paraffins and Hydrocarbon Types in Gasoline by Gas Chromatography," Anal. Chem., 35(12), 1918-1920 (1963).

32. Sanders, W. N., and J. B. Maynard, Anal. Chem., 40(3), 327-353 (1968).

33. Soulages, L., and M. Antonio, J. Chromatog. Sci., 9, 492-496 (1971).

34. Maczek, A. O. S., and C. S. G. Phillips, J. Chromatog., 29, 15-23 (1967).

35. Sidorov, R. I., A. N. Denisenko and I. N. Agopova, Khimi Tekhnol. Toplivai Masel, 9, 65 (1964).

36. UOP Method 744-77, Universal Oil products Company, Des Plaines, Ill.

37. 1975 Annual Book of ASTM Standards, Part 23.

38. Karr, C., Jr., W. D. Weatherford and R. G. Capell, Anal. Chem., 26, 252 (1954).

39. Lumpkin, H. E., and B. H. Johnson, ibid, pp. 1719.

40. McKinney, C. M., and R. L. Hopkins, ibid, pp. 1460.

41. Coleman, H. J., C. J. Thompson, R. L. Hopkins, H. T. Rall, J. Chromatog., 20, 240 (1965).

42. Charlet, E. M., K. R. Lanneaw and F. B. Johnson, Anal. Chem., 26, 861 (1954).

43. Snyder, L. R., J. Chromatog., 5, 430 (1961).

44. Ibid 6, 21 (1961).

45. Snyder, L. R., Anal. Chem., 33, 1527 (1961).

46. Chumatkov, Y. I., and S. K. Lopotenko, Chromatographia, 8, 240 (1975).

47. Stevenson, Robert, J. Chromatog Sci., 9, 257-262 (1971).

48. Hirsch, D. E., R. L. Hopkins, H. J. Coleman, F. O. Cotton, and C. J. Thompson, Anal. Chem., 44, 915 (1972).

49. Suatoni, J. C., H. R. Garber and B. E. Davis, J. Chromatog. Sci., 13, 367-371 (1975).

50. Suatoni, J. C., and R. E. Swab, J. Chromatog. Sci., 14, 535 (1976).

51. Fodor, G. E., and F. M. Newman, The Application of High-Performance Liquid Chromatography to the Analysis of Petroleum Materials. Part 2. Quantitative Hydrocarbon-Type Analysis of Middle Distillate Fuels. Southwest Research Institute, San Antonio, Texas. U.S. Army Research and Development Center, Ft. Belvoir, Virginia, Contract No. DAAK02-73-C-0221, May 1975.

52. ASTM D2425, Part 24, 1975 ASTM Annual Book of Standards.

53. Hunt, R. A., Jr., Ind. Eng. Chem., 45, 602 (1953).

54. Martel, C. R., and L. C. Angello, AF Aero Propulsion Laboratory. Technical Report AFAPL-TR-72-103 (May 1973).

55. Angello, L. C., AF Aero Propulsion Laboratory. Technical Report AFAPL-TR-74-76 (March 1974).